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NATIONAL STANDARD
REFERENCE DATA SYSTEM

Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States

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[1]Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington,D.C. 20234.
[2]Some divisions within the center are located at Boulder, Colorado, 80303.

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Compilation of Rate Constants
for the Reactions of Metal Ions
in Unusual Valency States

George V. Buxton and Robin M. Sellers

Cookridge Radiation Research Centre,
Cookridge Hospital,
Leeds LS16 6QB,
Great Britain

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

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The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

ERNEST AMBLER, *Director*

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Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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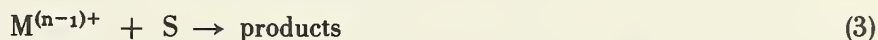
George V. Buxton and Robin M. Sellers**

Cookridge Radiation Research Centre, Cookridge Hospital,
Leeds LS16 6QB, Great Britain.

Kinetic data have been compiled for reactions of uncommon oxidation states of metals which are produced by radiolysis of aqueous solutions of metal ions. Most of the reaction rates are for transient species, and the rates were determined by pulse radiolysis; some data were obtained by flash photolysis and gamma radiolysis. Metal ions from Groups IB, IIB, IIIA, IVA, VIB, VIIB, VIIIB, and the lanthanides are included in the compilation.

Key words: Aqueous solution; chemical kinetics; complex ions; electron transfer; metal ions; radiation chemistry; rates; transients..

Introduction

The discovery of the hydrated electron as a major product of the radiolysis of water and the development of pulse radiolysis have together resulted in the accumulation, during the last ten years, of a considerable amount of information on the chemistry of unusual valency states of metal ions in aqueous solution, which has been reviewed recently (G. V. Buxton and R. M. Sellers, 77–0121).[1] For the most part attention has been focussed on hyper-reduced states produced in reaction (1), which affords a simple, and often unique, method of their formation. Reactions of hydroxyl radicals and hydrogen atoms, and of simple radicals derived from them, with metal ions have been less commonly studied.

$$e_{aq}^- + M^{n+} \rightarrow M^{(n-1)+} \tag{1}$$

$$2M^{(n-1)+} \rightarrow M^{n+} + M^{(n-2)+} \tag{2}$$

$$M^{(n-1)+} + S \rightarrow \text{products} \tag{3}$$
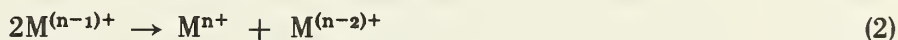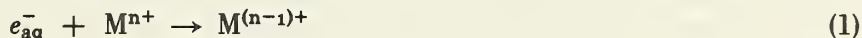
This compilation lists the rate constants for reactions of these metal ions in unusual valency states. In the majority of cases the species are unstable, generally decaying by dismutation (2), or reaction with the solvent or a solute (3). This instability has been the principal criterion on which the decision to include data in this tabulation has been based. However, because the bulk of information on these metal ions has been obtained by pulse radiolysis methods, we have also included some rate constants for the reactions of stable metal ions such as Cu^+, Cr^{2+} and Eu^{2+} measured by these methods. In these examples, indicated in the tables, much other data not recorded here has been obtained by other techniques.

[1]Literature references are given at the end of this paper.

Arrangement of the Tables

The tables are listed in alphabetical order of the chemical symbols of the metals involved. Within each table the arrangement is by oxidation state, starting with the lowest, and is further subdivided according to the complexing ligands in the order aquo ions (and hydrolysed forms), inorganic ligands in alphabetical order of the first letter of the chemical symbol of the principal element of that ligand (e.g. N for ammonia), and organic ligands in alphabetical order of their written names. For each individual transient species the reactants are in the order: inorganic species, organic radicals, both in alphabetical order of their chemical symbols, followed by organic compounds in alphabetical order of their written names.

Table 25 is somewhat different, and lists the rate constants for some intramolecular electron transfer reactions. The reactions are subdivided according to the method of production of the transient species. Note that all the rate constants in this table are first order, and have therefore units of s^{-1}. Reactions of metallo–proteins and related compounds are not dealt with in this compilation.

The data given for each reaction are the measured rate constant, and a brief description of the experimental conditions etc. as outlined below. Literature data published to approximately mid–1976 are covered.

Reaction: Three main methods have been used to measure the rate constants reported here:

    (i)   by monitoring the rate of removal of the absorption of the
                  metal species at some convenient wavelength
    (ii)   by monitoring the rate of formation of some product
    (iii)   by competition kinetics.

Methods (i) and (iii) have the disadvantage that they do not involve characterisation of the products of the reaction, and in many instances in the literature no additional experiments have been performed to overcome this. Often the reaction type has been assumed. Particular attention has been given to this problem in this compilation. Where there is no experimental information on the products given in the original work or elsewhere, only the left hand side of the equation is given, followed in brackets by the possible type of reaction as originally suggested, or as seems appropriate. If experimental evidence is given, the products are quoted, and the nature of the evidence indicated in the column headed 'Comments'.

In some cases the reactive intermediates themselves have not been fully characterised, and in such instances brief details of the method and conditions of formation are given.

Rate Constants: Most of the rate constants listed were measured under conditions where the reaction obeyed first order kinetics and no knowledge of absolute concentrations of the *transient* species is required. Error limits on the rate constants are those quoted in the original work. In the great majority of cases their magnitude is $\pm$ 10 – 15% of the rate constant value, which is typical of the precision of the mean of pseudo first order rate constants measured by pulse methods. If the data source gives no errors none are shown here, but they should be assumed to be at least $\pm$ 25% to allow for the possibility that the rate constant is derived from a single measurement.

Second order rate constants are prefaced by "$2k =$" or "$2k/\epsilon_\lambda =$" as appropriate. In cases where it is not clear whether the value refers to $2k$ or k this is noted in the 'Comments' column. The measured quantity is $2k/\epsilon_\lambda$ and is subject to the same limitations given above for pseudo first order rate constants. Calculation of $2k$ requires a knowledge of ϵ_λ, and where this quantity is quoted in the original work it is given under 'Comments'. In many instances, however, the values of ϵ_λ used to calculate $2k$ have not been clearly stated.

Evaluation of ϵ_λ requires a knowledge of the concentration of transient species present which, in radiation chemical systems, means that the dose per pulse and the G value[2] of the species must be known. In our experience these quantities are each likely to be uncertain by $\pm$ 10%, so that the error in $2k$ may be as much as three times as large as the error in $2k/\epsilon_\lambda$. Therefore, in the absence of any quoted errors, the error in $2k$ should be assumed to be $\pm$ 50%.

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[2]G is the number of molecules of a species produced per 100 eV of absorbed energy.

Equilibrium constants are quoted under the 'Rate Constants' heading, and are prefixed by "$K =$" followed by the appropriate units. If the individual rate constants for the forward and reverse processes are known these are shown as "k_f" and "k_r" respectively. Activation energies are prefaced by "$E_a =$" and are given in units of kJ mol^{-1}.

Ionic Strength (I): Ionic strengths have either been taken directly from the original work, or calculated from the conditions given. In the few instances where the formation of ion pairs has been taken into account the values are followed by an asterisk. If insufficient information is given to enable the ionic strength to be calculated the column has been left blank. The ionic strength of rate constants extrapolated to zero ionic strength is given as "$\rightarrow$ 0". Unfortunately in a number of studies little or no attempt has been made to maintain the ionic strength constant. The practice of many reaction kineticists of adding a high concentration of inert electrolyte, such as $NaClO_4$, has not been widely adopted by radiation chemists, no doubt because of possible complications due to direct radiolysis of the electrolyte (cf. J. Konstantatos and D. Katakis, 67–0019). There is no reason however why an ionic strength of say 0.1 or 0.5 mol dm^{-3} should not become standard for pulse radiolytic measurements. It is to be hoped that more consideration will be given to this problem in future studies.

Temperature: Where temperatures are quoted in the original work these have been given. In the absence of any information temperatures are given as room temperature (RT). The temperature ranges over which activation parameters have been measured are given as appropriate. Since many of the rate constants quoted in these tables are near the diffusion controlled limit and have therefore small activation energies, little uncertainty is engendered by an imprecise knowledge of the temperature. For example a change in temperature of 5° from 25° changes k by 11% for an activation energy of 16 kJ mol^{-1}.

Comments: Information and comments relevant to the reactions and rate constants are given in this column as outlined above. No attempt has been made to give a complete description of the conditions employed in the measurement of the rate constants quoted, but where the concentration of one or more of the solutes exceeds 0.1 mol dm^{-3} this has been noted.

References: The references are listed following the tables in order of the serial number of the paper in the files of the Radiation Chemistry Data Centre at the University of Notre Dame. The first two digits of this number represent the year in which the work was published. The references in the tables also give the first four letters of the first author's name and a dot for each additional author up to a maximum of four dots.

List of Abbreviations

Reaction:	af	adduct formation
	dis	dismutation (disproportionation)
	et	electron transfer
	int et	intramolecular electron transfer
	O at	oxygen atom transfer
	pt	proton transfer
	et – is	inner sphere electron transfer
	?	uncertain
Rate Constant:	$2k$	rate constant for second order reaction
	ϵ_λ	extinction coefficient at wavelength λ
	E_a	activation energy (units kJ mol^{-1})
	K	equilibrium constant
	pK	acid dissociation constant ($= -\log_{10}K$)
	k_f	rate constant for forward reaction of equilibrium
	k_r	rate constant for reverse reaction of equilibrium
	?	value uncertain
Ionic Strength:	$\rightarrow 0$	extrapolated to zero ionic strength
(I)	*	calculated taking into account the formation of ion pairs
	var	various
Temperature:	RT	room temperature
pH:	nat	natural pH of the solution
Method:	comp.	competition kinetics
	f.ph.	flash photolysis
	γ	γ–radiolysis
	pr	pulse radiolysis
Chemical Symbols:	bpy	bipyridyl
	en	ethylenediamine
	gly	glycine
	EDTA^{4-}	ethylenediamine tetraacetate
	NAD$^+$	nicotinamide adenine dinucleotide
	NTA^{3-}	nitrilotriacetate
	PNDA	p–nitroso–N,N–dimethylaniline
	L	ligand (specified in table).

TABLE 1. Silver(0) and Silver(II) reactions

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Ag(0) – aquo ions and complexes							
1.1	$Ag^0 + Ag^+ \rightarrow Ag_2^+$	5.9×10^9	–	RT	–	pr	Product characterised by absorption spectrum and charge.	Puki..68–0431
		$(6.5 \pm 0.3) \times 10^9$	–	29	1.0	pr	–	Farh...73–1053
		$(5.2 \pm 0.3) \times 10^9$	–	29	1.0	pr	Measured at pressure of 6.72 kbar.	Farh...73–1053
1.2	$Ag_2^+ + Ag^+ \rightarrow Ag^{2+} + Ag_2^0$	3.8×10^9	$\rightarrow 0$	RT	–	pr	Products characterised by absorption spectrum.	Puki..68–0431
1.3	$Ag_2^0 + Ag^+ \rightarrow Ag_3^+$	$ca.10^8$	–	RT	–	pr	Product characterised by absorption spectrum.	Puki..68–0431
1.4	$Ag_2^0/Ag_2^+ + MnO_4^-$ (et)	1.2×10^{10}	0.003	RT	–	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65–0385
1.5	$Ag_2^+ + O_2$ (et or af)	3.8×10^8	–	RT	–	pr	Product uncertain, but transfers an electron to 1,4–benzoquinone (see Sell.76–1134).	Baxe..65–0393
1.6	$Ag_3^+ + 1,4–benzo–$ $quinone \rightarrow Ag_3^{2+}(?) +$ $(1,4–benzoquinone)^-$	$(1.5 \pm 0.3) \times 10^8$	–	25 ± 2	5.8	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Sell.76–1134
1.7	$Ag_3^+ + menaquinone \rightarrow$ $Ag_3^{2+}(?) + (menaquinone)^-$	slow	–	–	7.0	pr	Only 24% electron transfer, which may be due to side reactions. Solutions contained 1 mol dm^{-3} 2–methyl–2–propanol.	Rao.73–1047
	Ag(0) – ammine complexes							
1.8	$Ag^0 + Ag(NH_3)_2^+ \rightarrow$ $Ag_2(NH_3)_n^+$	5.2×10^9	–	RT	–	pr	Ag^0 generated from $e_{aq}^- + Ag(NH_3)_2^+$ – might be same as product of $e_{aq}^- + Ag^+$. Product contains unknown number of ammine ligands.	Puki.68–0435
1.9	$Ag_2(NH_3)_n^+ + Ag_2(NH_3)_n^+ \rightarrow$ $Ag_4(NH_3)_n^{2+}$?	$2k = 2.6 \times 10^{10}$	–	RT	–	pr	Product uncertain; gives ultimately Ag_3^0.	Puki.68–0435
1.10	$Ag_2(NH_3)_n^+ + Ag(NH_3)_2^+ \rightarrow$ $Ag_3(NH_3)_n^{2+}$?	10^8	–	RT	–	pr	Measured from rate of formation of product, nature of which is uncertain.	Puki.68–0435
	Ag(II) – aquo complex							
1.11	$Ag^{2+} + Ag^{2+} \rightarrow$ $Ag^+ + Ag^{3+}$	1.5×10^9	–	RT	–	pr	–	Puki..68–0431
1.12	$Ag^{2+} + anisole \rightarrow$ $Ag^+ + anisole^+$	$(3.8 \pm 0.4) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171

TABLE 1. Silver(0) and Silver(II) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1\ a}$	I	$t/°\text{C}$	pH	Method	Comments	Ref.
1.13	Ag^{2+} + 1,2–dimethoxy–benzene $\rightarrow$ Ag^+ + (1,2–dimethoxybenzene)$^+$	$(6.0 \pm 0.6) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171
1.14	Ag^{2+} + 1,3–dimethoxy–benzene $\rightarrow$ Ag^+ + (1,3–dimethoxybenzene)$^+$	$(6.3 \pm 0.6) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171
1.15	Ag^{2+} + 1,4–dimethoxy–benzene $\rightarrow$ Ag^+ + (1,4–dimethoxybenzene)$^+$	$(4.6 \pm 0.5) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171
1.16	Ag^{2+} + 1,2,3–trimethoxybenzene $\rightarrow$ Ag^+ + (1,2,3–trimethoxybenzene)$^+$	$(2.5 \pm 0.3) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171
1.17	Ag^{2+} + 1,2,4–trimethoxybenzene $\rightarrow$ Ag^+ + (1,2,4–trimethoxybenzene)$^+$	$(7.0 \pm 0.7) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171
1.18	Ag^{2+} + 1,3,5–trimethoxybenzene $\rightarrow$ Ag^+ + (1,3,5–trimethoxybenzene)$^+$	$(5.6 \pm 0.6) \times 10^7$	–	20 ± 2	nat(?)	pr	Product characterised by absorption spectrum and esr.	O'Ne..75–1171

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 2. Gold(0) and Gold(II) reactions

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1\ a}$	I	$t/°\text{C}$	pH	Method	Comments	Ref.
	Au(0) from $Au(CN)_2^-$ + e_{aq}^-							
2.1	Au^0 + Au^0 $\rightarrow$ Au_2^0	$(3.2 \pm 0.9) \times 10^9$	0.001	RT	11	pr	Product assumed.	Ghos.68–0302
		$(2.9 \pm 0.7) \times 10^9$	0.1	RT	13	pr	Solutions contained 9.8×10^{-2} mol dm^{-3} H$_2$.	Ghos.68–0302
2.2	Au^0 + $Fe(CN)_6^{3-}$ (et?)	5.5×10^8	–	RT	–	pr	–	Ghos.68–0302
2.3	Au^0 + N_2O (et or O at)	5.5×10^8	–	RT	–	pr	–	Ghos.68–0302
2.4	Au^0 + O_2 (et or af)	3.6×10^9	–	RT	–	pr	–	Ghos.68–0302
	Au(0) from $Au(CN)_2^-$ + H							
2.5	Au^0 + Au^0 $\rightarrow$ Au_2^0	$(5.0 \pm 1.0) \times 10^9$	0.015	RT	2	pr	–	Ghos.68–0302
	Au(II) from $Au(CN)_2^-$ + OH							
2.6	Au^{II} + Au^{II} (dis or af)	$(2.4 \pm 0.6) \times 10^8$	0.01	RT	2	pr	Solutions contained 0.1 mol dm^{-3} HCl.	Ghos.68–0302
		$(4.8 \pm 1.2) \times 10^8$	0.01	RT	4,7	pr	Solutions contained 0.01 mol dm^{-3} KCl.	Ghos.68–0302
	Au(II) from $AuCl_4^-$ + H							
2.7	Au^{II} + Au^{II} $\rightarrow$ Au^I + Au^{III}	$(1.4 \pm 0.3) \times 10^9$	0.01	20	2	pr	Nature of products –see ref. 70–0580.	Baxe.70–0580
		$(8.6 \pm 0.7) \times 10^8$	0.011	20	2	pr	Solutions contained 10^{-3} mol dm^{-3} Cl$^-$.	Baxe.70–0580
		$(1.2 \pm 0.1) \times 10^9$	0.131	20	2	pr	Solutions contained 10^{-3} mol dm^{-3} Cl$^-$ + 0.12 mol dm^{-3} NaClO$_4$.	Baxe.70–0580
		$(2.7 \pm 0.6) \times 10^8$	0.02	20	2	pr	Solutions contained 10^{-2} mol dm^{-3} Cl$^-$.	Baxe.70–0580
		$(2.5 \pm 0.2) \times 10^7$	0.11	20	2	pr	Solutions contained 10^{-1} mol dm^{-3} Cl$^-$.	Baxe.70–0580

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 3. Cd(I) reactions

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
	Cd_{aq}^+							
3.1	Cd$^+$ + BrO$_3^-$ (et)	$(1.25 \pm 0.2) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
		$E_a = 13.4 \pm 1.7$ kJ mol^{-1}	0.08	3 – 90	nat	pr	–	Meye.70–1228
3.2	Cd$^+$ + Cd$^+$ → Cd$_2^{2+}$	$2k = ca.\ 1.2 \times 10^9$	0.4	25±2	nat	pr	Measured at 300 nm taking $\epsilon_{300} = 8080$ dm^3 mol^{-1} cm^{-1}. Rate constant es–timated from studies of Cd$^+$ decay in pre–sence of several different OH scav–engers.	Buxt.75–1027
		$2k = 3.0 \times 10^9$	0.002	RT	nat	pr	Measured at 300 nm taking $\epsilon_{300} = 16500$ dm^3 mol^{-1} cm^{-1}. Rate constant estimated from computer analy–sis of Cd$^+$ decay. Competing reactions taken to be Cd$^+$ + H$_2$O$_2$ and Cd$^+$ + R· (R = CH$_3$COHCH$_3$, CH$_3$CHOH, CH$_2$OH). Pro–duct identified from effect of ionic strength on its decay.	Kelm..75–1064
		$2k = 5.0 \times 10^9$	0.004	RT	nat	pr	Measured at 313 nm taking $\epsilon_{301} = 14000$ dm^3 mol^{-1} cm^{-1}. Rate constant in–dependent of OH scavenger used.	Bark.75–1153
3.3	Cd$^+$ + Co(en)$_3^{3+}$ (et)	$(1.6 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.4	Cd$^+$ + cis-Co(en)$_2$Cl$_2^+$ (et)	$(2.3 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.5	Cd$^+$ + trans-Co(en)$_2$Cl$_2^+$ (et)	$(2.6 \pm 0.4) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.6	Cd$^+$ + Co(en)$_2$CO$_3^+$ (et)	$(6.7 \pm 1.0) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.7	Cd$^+$ + cis-Co(en)$_2$F$_2^+$ (et)	$(6.0 \pm 0.9) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.8	Cd$^+$ + Co(en)$_2$FH$_2$O^{2+} (et)	$(4.1 \pm 0.6) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.9	Cd$^+$ + cis-Co(en)$_2$NH$_3$Cl^{2+} (et)	$(1.75 \pm 0.26) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.10	Cd$^+$ + cis-Co(en)$_2$NH$_3$NO$_2^{2+}$ (et)	$(2.8 \pm 0.7) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.11	Cd$^+$ + Co(NH$_3$)$_6^{3+}$ (et)	$(1.72 \pm 0.3) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.12	Cd$^+$ + Co(NH$_3$)$_5$Br^{2+} (et)	$(25 \pm 0.4) \times 10^9$	0.08	RT	4.0	pr	–	Meye.69–0428
3.13	Cd$^+$ + Co(NH$_3$)$_5$Cl^{2+} (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.14	Cd$^+$ + Co(NH$_3$)$_5$CN^{2+} (et)	$(9.1 \pm 1.4) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.15	Cd$^+$ + Co(NH$_3$)$_5$F^{2+} (et)	$(5.4 \pm 0.8) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
3.16	Cd$^+$ + Co(NH$_3$)$_5$fumarate$^+$ (et or af?)	$(8.3 \pm 2.1) \times 10^8$	0.08	RT	5–6	pr	Products of the reaction have re–latively large ab–sorption.	Meye.69–0428
3.17	Cd$^+$ + Co(NH$_3$)$_5$H$_2$O^{3+} (et)	$(6.2 \pm 0.9) \times 10^8$	0.08	RT	4.0	pr	–	Meye.69–0428

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TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
3.18	$Cd^+ + Co(NH_3)_5OH^{2+}$ (et)	$(9.0 \pm 1.3) \times 10^8$	0.08	RT	7.1	pr	–	Meye.69–0428
3.19	$Cd^+ + Co(NH_3)_5N_3^{2+}$ (et)	$(1.41 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.20	$Cd^+ + Co(NH_3)_5NCS^{2+}$ (et)	$(1.32 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
3.21	$Cd^+ + Co(NH_3)_5OOCCH_3^{2+}$ (et)	$(9.0 \pm 1.3) \times 10^7$	0.08	RT	5–6	pr	–	Meye.69–0428
3.22	$Cd^+ + Cr^{3+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
3.23	$Cd^+ + CrO_4^{2-}$ (et)	$(9.8 \pm 1.0) \times 10^9$	0.02*	25±2	nat	pr	–	Buxt..76–1072
3.24	$Cd^+ + Cr_2O_7^{2-}$ (et)	$(1.6 \pm 0.2) \times 10^{10}$	0.02*	25±2	nat	pr	–	Buxt..76–1072
3.25	$Cd^+ + Cu^{2+}$ (et)	$(1.2 \pm 0.2) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
		$(1.1 \pm 0.2) \times 10^9$	0.04	RT	5–8	γ	Measured by competition kinetics using NO_3^- as competitor and taking $k(Cd^+ + NO_3^-) = 3.5 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$.	Fiti70–0117
3.26	$Cd^+ + H_2O_2 \rightarrow$ $Cd^{2+} + OH + OH^-$	$(1.55 \pm 0.2) \times 10^9$	–	RT	nat	pr	–	Meye.68–0855
		$(2.2 \pm 0.2) \times 10^9$	–	25	nat	pr	–	Buxt..76–1072
		2.8×10^9	–	RT	nat	pr		Buxt..67–0062
		$E_a = 9.2 \pm 0.8$ $kJ\ mol^{-1}$	–	1 – 30	nat	pr	–	Buxt..76–1072
							Products identified in γ–radiolysis studies (see Buxt.. 73–0039).	
3.27	$Cd^+ + H_3O^+$	$< 10^6$	0.08	RT	–	pr	–	Meye.68–0855
3.28	$Cd^+ + IO_3^-$ (et)	$(2.3 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	–	Meye.68–0855
		$(2.1 \pm 0.2) \times 10^9$	0.04	RT	5–8	γ	Measured by competition kinetics using NO_3^- as competitor and taking $k(Cd^+ + NO_3^-) = 3.5 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$.	Fiti70–0117
3.29	$Cd^+ + MnO_4^-$ (et)	$(7.8 \pm 0.8) \times 10^9$	–	ca.22	7.0	pr	Measured by the rate of depletion of the MnO_4^- absorption in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
		1.3×10^{10}	ca. 0.004	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65–0385
3.30	$Cd^+ + Ni^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
3.31	$Cd^+ + NO_2^-$ (et)	$(2.0 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	–	Meye.68–0855
		$E_a = 12.5 \pm 1.7$ $kJ\ mol^{-1}$	0.08	3 – 90	nat	pr	–	Meye.70–1228
3.32	$Cd^+ + NO_3^-$ (et)	$(3.5 \pm 0.5) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
3.33	$Cd^+ + N_2O \rightarrow CdO^+ + N_2$	$< 2 \times 10^6$	–	RT	nat	pr	–	Meye.68–0855
		1×10^6	–	RT	nat	pr	–	Buxt..67–0062
		$(3.5 \pm 0.4) \times 10^6$	–	25	nat	pr	Solutions contained 0.1 mol dm^{-3} methanol. Products inferred from γ–ray induced chain reaction in the system $Cd^{2+} + HCO_2^- + N_2O$. $G(N_2)$ measured in the system $Cd^{2+} + N_2O$. (see ref. 73–0039).	Buxt..76–1072
		$E_a = 45.6 \pm 1.3$ kJ mol^{-1}	–	1 – 30	nat	pr		
3.34	$Cd^+ + O_2$ (et or af)	$(2.4 \pm 0.4) \times 10^9$	–	RT	nat	pr	–	Meye.68–0855
		3.3×10^9	–	RT	nat	pr	–	Baxe..66–0848
		$(3.6 \pm 0.4) \times 10^9$	–	25±2	nat	pr	Absorption spectrum of products similar to that of O_2^-; but decay slower (see ref. 76–1072). Product transfers an electron to p–benzoquinone (see ref. 76–1134). Evidence possibly indicates product to be CdO_2^+.	Buxt..76–1072
3.35	$Cd^+ + OH \rightarrow Cd^{2+} + OH^-$	$ca.\ 8 \times 10^9$	–	25	nat	pr	Estimated from decay of Cd^+ in absence of OH scavengers taking into account the major competing reaction $Cd^+ + Cd^+$.	Buxt.75–1027
		1.8×10^{10}	–	RT	nat	pr	Experimentally determined rate constant for the decay of Cd^+ in the absence of OH scavengers. Not corrected for $Cd^+ + Cd^+$ or other competing reactions.	Baxe..66–0848
		2×10^{10}	–	RT	nat	pr	Estimated from computer analysis of the decay of the optical absorption and conductivity of Cd^+ in the absence of OH scavengers, taking $Cd^+ + Cd^+$ and $Cd^+ + H_2O_2$ as the competing reactions. Products identified from conductivity changes.	Kelm..75–1064

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TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
3.36	$Cd^+ + Pb^{2+}$ (et)	7.5×10^7	–	RT	nat	pr	–	Baxe..66–0848
3.37	$Cd^+ + Ru(NH_3)_6^{3+}$ (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	–	Nav..70–1229
3.38	$Cd^+ + S_2O_8^{2-} \rightarrow$ $Cd^{2+} + SO_4^- + SO_4^{2-}$	$(2.4 \pm 0.2) \times 10^9$	0.02*	25±2	nat	pr	Product identification: SO_4^- observed to form at same rate as Cd^+ decayed.	Buxt..76–1072
3.39	$Cd^+ + Zn^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
3.40	$Cd^+ + \cdot CH_2OH \rightarrow CdCH_2OH^+$	2×10^8	–	RT	nat	pr	Product inferred from conductivity measurements.	Kelm..75–1064
3.41	$Cd^+ + CH_3CHOH \rightarrow$ $CdCH_3CHOH^+$	$< 2 \times 10^8$ $(1.3 \pm 0.7) \times 10^9$	– –	RT RT	nat nat	pr pr	– Product inferred from conductivity measurements.	Bark.75–1153 Kelm..75–1064
3.42	$Cd^+ + \cdot CHOHCH_2OH$	$< 2 \times 10^8$	–	RT	nat	pr	–	Bark.75–1153
3.43	$Cd^+ + CH_3COHCH_3 \rightarrow$ $CdCH_3COHCH_3^+$	$< 2 \times 10^8$ $(2.4 \pm 1.2) \times 10^9$	– –	RT RT	nat nat	pr pr	– Product inferred from conductivity measurements.	Bark.75–1153 Kelm..75–1064
3.44	$Cd^+ + \cdot CHOHCHOHCH_2OH$	$< 2 \times 10^8$	–	RT	nat	pr	–	Bark.75–1153
3.45	$Cd^+ + \cdot CH_2(CH_3)_2COH \rightarrow$ $Cd^{2+} + (CH_3)_2C{=}CH_2 + OH^-$	$ca.\ 1 \times 10^9$ $< 2 \times 10^8$	– –	RT RT	nat nat	pr pr	Isobutene detected as product. –	Kelm..75–1064 Bark.75–1153
3.46	$Cd^+ + {-}(CH_2CH_2O)_n(CHCH_2O){-}$	$< 2 \times 10^8$	–	RT	nat	pr	Radical from polyethylene glycol (mw 10^4) + OH.	Bark.75–1153
3.47	$Cd^+ +$ allyl alcohol	$\leqslant 5 \times 10^7$	–	25±2	nat	pr	–	Buxt..76–1072
3.48	$Cd^+ +$ 9,10–anthraquinone $\rightarrow Cd^{2+} +$ (9,10–anthraquinone)$^-$	$(1.03 \pm 0.1) \times 10^9$	–	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
3.49	$Cd^+ +$ benzophenone $\rightarrow$ $Cd^{2+} +$ (benzophenone)$^-$	1.0×10^9	–	RT	7.0	pr	Measured by the rate of formation of the ketyl radical in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.75–1032
3.50	$Cd^+ +$ 1,4–benzoquinone $\rightarrow$ $Cd^{2+} +$ (1,4–benzoquinone)$^-$	$(4.1 \pm 0.8) \times 10^9$	–	25±2	5.4	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Sell.76–1134
		4.4×10^9	–	RT	7.0	pr	Measured in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.75–1032
		$(7.7 \pm 0.8) \times 10^9$	–	ca.22	7.0	pr	Measured in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104

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TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
3.51	$Cd^+ + $ 2-hydroxy-1,4–naphthoquinone $\rightarrow$ $Cd^{2+} + $ (2-hydroxy-1,4–naphthoquinone)$^-$	$(3.57 \pm 0.4) \times 10^9$	–	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
3.52	$Cd^+ + $ menaquinone $\rightarrow$ $Cd^{2+} + $ (menaquinone)$^-$	$(4.6 \pm 0.5) \times 10^9$	–	RT	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1047, Rao.75–1032
		$(4.68 \pm 0.5) \times 10^9$	–	ca. 22	7.0	pr	Measured in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
3.53	$Cd^+ + $ NAD$^+ \rightarrow$ $Cd^{2+} + $ NAD·	$(2.9 \pm 0.3) \times 10^9$	–	ca. 22	7.0	pr	Measured by the rate of formation of NAD· in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
3.54	$Cd^+ + $ 1,4–naphthoquinone-2–sulphonate $\rightarrow$ $Cd^{2+} + $ (1,4–naphthoquinone-2–sulphonate)$^-$	$(7.35 \pm 0.7) \times 10^9$	–	ca. 22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
3.55	$Cd^+ + $ PNDA (et)	1.4×10^{10}	–	RT	nat	pr	–	Dain.68–0066
3.56	$Cd^+ + $ riboflavin $\rightarrow$ $Cd^{2+} + $ (riboflavin)$^-$	$(5.10 \pm 0.5) \times 10^9$	–	ca. 22	7.0	pr	Measured by the rate of formation of the reduced riboflavin in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
	Cd(I) complexes *CdEDTA^{3-}*							
3.57	CdEDTA$^{3-} + $ BrO$_3^-$ (et)	$(8.9 \pm 1.8) \times 10^6$	0.16	RT	11.3	pr		Meye.70–1228
		$E_a = 4.6 \pm 1.2$ kJ mol^{-1}	0.16	3–90	11.3	pr	–	Meye.70–1228
3.58	CdEDTA$^{3-} + $ CdEDTA^{3-} (et or af)	$'k'/\epsilon_{350} = (5.8 \pm 1.5) \times 10^3$ cm s^{-1}	0.16	RT	11.3	pr	Unclear whether k or $2k$.	Meye.70–1228
		$'k' = (4 \pm 2) \times 10^7$	0.16	RT	11.3	pr	Unclear whether k or $2k$.	Meye.70–1228
3.59	CdEDTA$^{3-} + $ IO$_3^-$ (et)	$(2.7 \pm 0.6) \times 10^8$	0.16	RT	11.3	pr	–	Meye.70–1228
3.60	CdEDTA$^{3-} + $ NO$_2^-$ (et)	$(3.2 \pm 0.6) \times 10^8$	0.16	RT	11.3	pr	–	Meye.70–1228
		$E_a = 8.4 \pm 1.2$ kJ mol^{-1}	0.16	3 – 90	11.3	pr	–	Meye.70–1228
3.61	CdEDTA$^{3-} + $ NO$_3^-$ (et)	$(1.66 \pm 0.3) \times 10^7$	0.16	RT	11.3	pr	–	Meye.70–1228
	Cd(en)$_n^+$ (n unknown)							
3.62	Cd(en)$_n^+ + $ BrO$_3^-$ (et)	$(1.28 \pm 0.3) \times 10^8$	0.64	RT	11.4	pr	–	Meye.70–1228
3.63	Cd(en)$_n^+ + $ IO$_3^-$ (et)	$(2.5 \pm 0.5) \times 10^9$	0.64	RT	11.4	pr	–	Meye.70–1228
3.64	Cd(en)$_n^+ + $ NO$_2^-$ (et)	$(1.12 \pm 0.2) \times 10^9$	0.64	RT	11.4	pr	–	Meye.70–1228
3.65	Cd(en)$_n^+ + $ NO$_3^-$ (et)	$(4.5 \pm 0.9) \times 10^8$	0.64	RT	11.4	pr	–	Meye.70–1228

TABLE 3. Cd(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°\text{C}$	pH	Method	Comments	Ref.
	Cd(gly)							
3.66	$Cd(gly) + BrO_3^-$ (et)	$(6.1 \pm 1.2) \times 10^7$	0.21	RT	10.5	pr	–	Meye.70–1228
3.67	$Cd(gly) + IO_3^-$ (et)	$(1.8 \pm 0.4) \times 10^9$	0.21	RT	10.5	pr	–	Meye.70–1228
3.68	$Cd(gly) + NO_2^-$ (et)	$(8.5 \pm 1.7) \times 10^8$	0.21	RT	10.5	pr	–	Meye.70–1228
3.69	$Cd(gly) + NO_3^-$ (et)	$(2.4 \pm 0.5) \times 10^8$	0.21	RT	10.5	pr	–	Meye.70–1228
	CdNTA^{2-}							
3.70	$CdNTA^{2-} + BrO_3^-$ (et)	$(1.02 \pm 0.2) \times 10^7$	0.10	RT	10.7	pr	–	Meye.70–1228
3.71	$CdNTA^{2-} + CdNTA^{2-}$ (et or af)	$'k'/\epsilon_{350} = (1.2 \pm 0.4) \times 10^5$ cm s^{-1}	0.10	RT	10.7	pr	Unclear whether k or $2k$.	Meye.70–1228
		$'k' = (8 \pm 4) \times 10^8$	0.10	RT	10.7	pr	Unclear whether k or $2k$.	Meye.70–1228
3.72	$CdNTA^{2-} + IO_3^-$ (et)	$(6.1 \pm 1.2) \times 10^8$	0.10	RT	10.7	pr	–	Meye.70–1228
3.73	$CdNTA^{2-} + NO_2^-$ (et)	$(4.2 \pm 0.8) \times 10^7$	0.10	RT	10.7	pr	–	Meye.70–1228
3.74	$CdNTA^{2-} + NO_3^-$ (et)	$(4.5 \pm 0.9) \times 10^7$	0.10	RT	10.7	pr	–	Meye.70–1228
	Cd(I)–radical complexes							
3.75	$CdCH_3CHOH^+ + H_2O \rightarrow$ $Cd^{2+} + CH_3CH_2OH + OH^-$	257 s^{-1}	–	RT	nat	pr	Products inferred from conductivity measurements.	Kelm..75–1064
3.76	$CdCH_3COHCH_3^+ + H_2O \rightarrow$ $Cd^{2+} + CH_3CHOHCH_3 + OH^-$	161 s^{-1}	–	RT	nat	pr	Products inferred from conductivity measurements.	Kelm..75–1064
3.77	$Cd_2^{2+} + \cdot CH_2(CH_3)_2COH \rightarrow$ $Cd^+ + Cd^{2+} + (CH_3)_2C{=}CH_2 + OH^-$	*ca.* 1×10^9	–	RT	nat	pr	Isobutene detected as product.	Kelm..75–1064

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 4. Cobalt(I) reactions

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Co^+_{aq}							
4.1	$Co^+ + Br_2^-$ (et)	$(1.0 \pm 0.3) \times 10^{10}$	–	RT	nat	f.ph.	Competing reactions $Br_2^- + Br_2^-$ and $Co^+ + Co^+$ not considered.	Thor.70–7726
4.2	$Co^+ + BrO_3^-$ (et)	$(4.8 \pm 0.5) \times 10^9$	0.019*	25±2	nat	pr	–	Buxt..76–1072
		$(7.1 \pm 1.1) \times 10^9$	→ 0	25±2	nat	pr	–	Buxt..76–1072
4.3	$Co^+ + Cd^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
4.4	$Co^+ + Co^+$ (et or af)	$2k < 4 \times 10^9$	0.019*	25±2	nat	pr	Estimated at 370 nm taking ϵ_{370} = 2080 $dm^3\ mol^{-1}\ cm^{-1}$.	Buxt.75–1027
4.5	$Co^+ + Cu^{2+}$ (et)	$(4.1 \pm 0.4) \times 10^8$	0.019*	25±2	nat	pr	–	Buxt..76–1072
		$(1.06 \pm 0.36) \times 10^{10}$	0.04	RT	5–8	γ	Measured by competition kinetics using NO_3^- as competitor and taking $k(Co^+ + NO_3^-) = 1.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$.	Fiti70–0117
4.6	$Co^+ + H_2O_2 \rightarrow$ $Co^{2+} + OH + OH^-$	$(1.6 \pm 0.2) \times 10^9$	–	25	nat	pr	–	Buxt..76–1072
		1.9×10^9	–	RT	nat	pr	–	Buxt..67–0062
		$E_a = 13.0 \pm 1.0$ $kJ\ mol^{-1}$	–	1 – 30	nat	pr	– Products identified in γ–radiolysis studies (see ref. 73–0039).	Buxt..76–1072
4.7	$Co^+ + IO_3^-$ (et)	$(4.3 \pm 0.4) \times 10^9$	0.019*	25±2	nat	pr	–	Buxt..76–1072
		$(4.9 \pm 0.8) \times 10^9$	0.04	RT	5–8	γ	Measured by competition kinetics using NO_3^- as competitor and taking $k(Co^+ + NO_3^-)$ = $1.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$.	Fiti70–0117
4.8	$Co^+ + MnO_4^-$ (et)	1.06×10^{10}	ca. 0.004	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65–0385
4.9	$Co^+ + N_2O \rightarrow CoO^+ + N_2$	7×10^8	–	RT	nat	γ	Estimated from N_2 yields in the γ–radiolysis of Co^{2+} + N_2O solutions.	Buxt..67–0062
		$(1.0 \pm 0.1) \times 10^9$	–	25±2	nat	pr	– Products inferred from γ–ray induced chain reaction in the system Co^{2+} + HCO_2^- + N_2O. (see ref. 73–0039).	Buxt..76–1072
4.10	$Co^+ + NO_3^-$ (et)	$(1.8 \pm 0.2) \times 10^9$	0.019	25±2	nat	pr	–	Buxt..76–1072
4.11	$Co^+ + Ni^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848

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TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [a]	I	$t/^{\circ}\mathrm{C}$	pH	Method	Comments	Ref.
4.12	$Co^+ + O_2$ (et or af)	$(6.0 \pm 0.6) \times 10^9$	–	25 ± 2	nat	pr	Absorption of products similar to that of O_2^- but decay slower (see ref. 76–1072). Product transfers an electron to 1,4–benzoquinone (see ref. 76–1134). Evidence possibly indicates product to be CoO_2^+.	Buxt..76–1072
4.13	$Co^+ + OH$ (et)	$ca.8 \times 10^9$	–	25 ± 2	nat	pr	Estimated from decay of Co^+ in absence of OH scavengers, taking into account the major competing reaction $Co^+ + Co^+$.	Buxt.75–1027
4.14	$Co^+ + Pb^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
4.15	$Co^+ + S_2O_8^{2-} \rightarrow$ $Co^{2+} + SO_4^- + SO_4^{2-}$	$(2.8 \pm 0.5) \times 10^9$	0.019	25 ± 2	nat	pr	Formation of SO_4^- inferred from the absorption produced on pulse radiolysis of solutions of $Co^{2+} + S_2O_8^{2-}$.	Buxt..76–1072
4.16	$Co^+ + Zn^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
4.17	$Co^+ + $ allyl alcohol $\rightarrow$ $(Co\text{–allyl alcohol})^+$	$ca.\ 10^6$	–	25 ± 2	nat	pr	Product characterised by its absorption spectrum.	Buxt..76–1072
4.18	$Co^+ + 9,10$–anthraquinone $\rightarrow Co^{2+} + (9,10$–anthraquinone)$^-$	$(1.05 \pm 0.1) \times 10^9$	–	$ca.\ 22$	nat	pr	Measured by the rate of formation of the semiquinone in the presence of $ca.\ 1\ \mathrm{mol\ dm^{-3}}$ 2–methyl–2–propanol.	Rao.73–1104
4.19	$Co^+ + $ benzophenone $\rightarrow$ $Co^{2+} + $ (benzophenone)$^-$	2.5×10^9	–	RT	7.0	pr	Measured by the rate of formation of the ketyl radical in the presence of $ca.\ 1\ \mathrm{mol\ dm^{-3}}$ 2–methyl–2–propanol.	Rao.75–1032
4.20	$Co^+ + 1,4$–benzoquinone $\rightarrow$ $Co^{2+} + (1,4$–benzoquinone)$^-$	4.8×10^9	–	RT	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of $ca.\ 1\ \mathrm{mol\ dm^{-3}}$ 2–methyl–2–propanol.	Rao.75–1032
		$(5.1 \pm 0.5) \times 10^9$	–	25 ± 2	4.7	pr	Measured in the presence of 1 mol $\mathrm{dm^{-3}}$ 2–methyl–2–propanol.	Sell.76–1134
		$(7.35 \pm 0.7) \times 10^9$	–	$ca.\ 22$	7.0	pr	Measured in the presence of $ca.\ 1$ mol $\mathrm{dm^{-3}}$ 2–methyl–2–propanol.	Rao.73–1104

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.21	$Co^+ +$ menaquinone $\rightarrow$ $Co^{2+} +$ (menaquinone)$^-$	$(4.0 \pm 0.4) \times 10^9$	–	RT	7.3	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1047 Rao.75–1032
		$(4.1 \pm 0.1) \times 10^9$	–	ca. 22	7.0	pr	Measured in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
4.22	$Co^+ +$ 1,4-naphthoquinone-2-sulphonate $\rightarrow Co^{2+} +$ (1,4-naphthoquinone-2-sulphonate)$^-$	$(6.83 \pm 0.7) \times 10^9$	–	ca. 22	7.3	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104
4.23	$Co^+ +$ riboflavin $\rightarrow$ $Co^{2+} +$ (riboflavin)$^-$	$(2.55 \pm 0.3) \times 10^9$	–	ca. 22	7.0	pr	Measured by the rate of formation of the reduced riboflavin in the presence of ca. 1 mol dm^{-3} 2-methyl-2-propanol.	Rao.73–1104

Co(I) complexes
$Co(CN)_5^{4-}$ (from $Co(CN)_5^{3-}$ + e_{aq}^-)

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.24	$Co(CN)_5^{4-} + H_2O \rightarrow$ $Co(CN)_5H^{3-} + OH^-$	$(1.1 \pm 0.1) \times 10^5\ s^{-1}$	–	20	ca. 13	pr	Measured in the presence of ca. 0.1 mol dm^{-3} H$_2$. Proton transfer mechanism implied from isotope effect (compare entry 4.25).	Vene.71–0097
4.25	$Co(CN)_5^{4-} + D_2O \rightarrow$ $Co(CN)_5D^{3-} + OD^-$	$(1.9 \pm 0.2) \times 10^4\ s^{-1}$	–	20	ca. 13	pr	Measured in D$_2$O in the presence of ca. 0.1 mol dm^{-3} H$_2$.	Vene.71–0097

CoL$^+$ (L = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.26	$CoL^+ + H_2O \rightarrow$ $CoLH^{2+} + OH^-$	20	0.001	RT	9–10	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.27	$CoL^+ + H_3O^+ \rightarrow$ $CoLH^{2+} + H_2O$	1.2×10^9	0.015	RT	3.5–4.2	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001

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TABLE 4. Cobalt(I) reactions — Continued

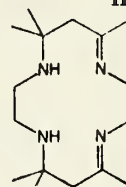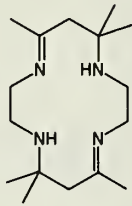| No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.28	$CoL^+ + H_2PO_4^- \rightarrow$ $CoLH^+ + HPO_4^{2-}$	3.0×10^7	0.005 –0.01	RT	5.5	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.29	$CoL^+ + N_2O$ (et)	9.0×10^6	0.01	RT	9.2	pr	Reaction possibly involves two electron oxidation to Co(III) complex.	Tait..76–1001
4.30	$CoL^+ + O_2 \rightarrow CoLO_2^+$	9.0×10^8	0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Reaction does not involve the formation of CoL^{2+}, assumed therefore to involve the coordination of the O_2.	Tait..76–1001

CoL^+ ($L = 5,7,7,12,14,14$–hexamethyl–$1,4,8,11$–tetraazacyclotetradeca–$4,11$–diene).

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.31	$CoL^+ + Co(bpy)_3^{3+}$ (et)	1.2×10^9	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.32	$CoL^+ + Co(en)_3^{3+}$ (et)	7.9×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.33	$CoL^+ + Co(NH_3)_6^{3+}$ (et)	7.5×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.34	$CoL^+ + CoL^{2+}$ (et)	4.0×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.35	$CoL^+ + CoL'^{2+}$ (et)	6.7×10^6	ca. 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001

($L' = 2,3,9,10$–tetramethyl–$1,4,8,11$–tetraazacyclotetradeca–$1,2,8,10$–tetraene)

| 4.36 | $CoL^+ + Cr(bpy)_3^{3+}$ (et) | 1.2×10^9 | ca. 0.02 | RT | 9.2 | pr | Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. | Tait..76–1001 |

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.37	$CoL^+ + Fe(bpy)_3^{3+}$ (et)	2.3×10^7	*ca.* 0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.38	$CoL^+ + H_2O \rightarrow$ $CoLH^{2+} + OH^-$	48	0.001	RT	9–10	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.39	$CoL^+ + H_3O^+ \rightarrow$ $CoLH^+ + H_2O$	3.1×10^9	0.015	RT	3.5–4.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.40	$CoL^+ + HPO_4^{2-} \rightarrow$ $CoLH^{2+} + PO_4^{3-}$	1.0×10^5	0.06–0.3	RT	10.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.41	$CoL^+ + H_2PO_4^- \rightarrow$ $CoLH^+ + HPO_4^{2-}$	9.8×10^7	0.005–0.01	RT	5.5	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.42	$CoL^+ + NH_4^+ \rightarrow$ $CoLH^+ + NH_3$	6.8×10^5	0.015–0.1	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.43	$CoL^+ + N_2O$ (et)	3.9×10^7	0.01	RT	9.2	pr	Reaction possibly involves two electron oxidation to Co(III) complex.	Tait..76–1001
4.44	$CoL^+ + O_2 \rightarrow CoLO_2^+$	1.7×10^9	0.02	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Reaction does not involve formation of CoL^{2+}, assumed therefore to involve the coordination of the O_2.	Tait..76–1001
4.45	$CoL^+ + Ru(NH_3)_6^{2+}$ (et)	4.0×10^8	0.016–0.028	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001

TABLE 4. Cobalt(I) reactions — Continued
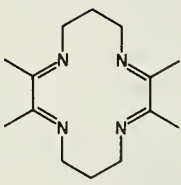
No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.46	$CoL^+ + Ru(NH_3)_5NO^{3+}$ (et)	3.9×10^7	0.016–0.028	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001
4.47	$CoL^+ +$ acetic acid → $CoLH^+ + CH_3COO^-$	7.5×10^7	0.01–0.05	RT	4.8	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.48	$CoL^+ +$ 9,10–anthraquinone –2–sulphonate → $CoL^{2+} +$ (9,10–anthraquinone–2–sulphonate)$^-$	4.4×10^9	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Semiquinone product characterised by its absorption.	Tait..76–1001
4.49	$CoL^+ +$ 3–benzoylpyridine (et + ?)	4.6×10^8	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Only 50% electron transfer to the 3–benzoylpyridine. Other reaction pathway(s) not characterised.	Tait..76–1001
4.50	$CoL^+ +$ fluorenone → $CoL^{2+} +$ (fluorenone)$^-$	4.3×10^9	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Ketyl radical product characterised by its absorption.	Tait..76–1001
4.51	$CoL^+ +$ menaquinone → $CoL^{2+} +$ (menaquinone)$^-$	4.6×10^9	0.004	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Semiquinone product characterised by its absorption.	Tait..76–1001
4.52	$CoL^+ +$ methyl iodide (et)	4.7×10^8	0.015	RT	9.2	pr	No evidence for substitution (S_N2) reaction pathway.	Tait..76–1001

CoL^+ ($L = 2,3,9,10$–tetramethyl–$1,4,8,11$–tetraazacyclotetradeca–$1,3,8,10$–tetraene)

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.53	$CoL^+ + Co(bpy)_3^{3+}$ (et)	8.5×10^7	0.016–0.028	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1001

TABLE 4. Cobalt(I) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
4.54	$CoL^+ + Cr(bpy)_3^{3+}$ (et)	1.6×10^8	0.016–0.028	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1001
4.55	$CoL^+ + H_3O^+ \rightarrow$ $CoLH^{2+} + H_2O$	1.6×10^5	0.06–0.6	RT	0.25–1.25	pr	Measured in the presence of 2 mol dm^{-3} 2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.56	$CoL^+ + O_2 \rightarrow CoLO_2^+$	1.1×10^9	0.02	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. Reaction does not involve formation of CoL^{2+}, assumed therefore to involve the coordination of O_2.	Tait..76–1001
4.57	$CoL^+ + $ acetic acid $\rightarrow$ $CoLH^{2+} + CH_3COO^-$	6.2×10^4	0.01–0.05	RT	4.8	pr	Measured in the presence of 2 mol dm^{-3} 2-propanol. See ref. for evidence for proton transfer mechanism.	Tait..76–1001
4.58	$CoL^+ + $ 9,10-anthraquinone-2,6-sulphonate $\rightarrow CoL^{2+}$ $+$ (9,10-anthraquinone-2,6-sulphonate)$^-$	3.8×10^9	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. Semiquinone product characterised by its absorption.	Tait..76–1001
4.59	$CoL^+ + $ indigosulphonate $\rightarrow$ $CoL^{2+} + $ (indigosulphonate)$^-$	4.9×10^9	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. Radical anion product characterised by its absorption.	Tait..76–1001
4.60	$CoL^+ + $ riboflavin $\rightarrow$ $CoL^{2+} + $ (riboflavin)$^-$	1.0×10^9	0.004	RT	6.5	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol. Radical anion product characterised by its absorption.	Tait..76–1001

[a] If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Cr(I) Reactions Cr_{aq}^+							
5.1	$Cr^+ + H_2O$	$< 5 \times 10^5\,\text{s}^{-1}$	–	22 ± 2	3.0–4.3	pr	Estimated from first order, dose dependent decay of Cr^+. Major competing reactions thought to be $Cr^+ + H_2O_2$. H_2 detected as product ($G = 2.9$ at pH 3.4).	Cohe.74–1142
	CrH^{2+} *(from $H + Cr^{2+}$)*							
5.2	$CrH^{2+} + H_2O$	$< 1\,\text{s}^{-1}$	–	22 ± 2	0–2	pr	–	Cohe.74–1142
5.3	$CrH^{2+} + H_3O^+ \rightarrow$ $Cr^{3+} + H_2 + H_2O$	$(1.8 \pm 0.2) \times 10^4$	var	22 ± 2	0–2	pr	$G(H_2) = 3.8$ at pH 0–2.	Cohe.74–1142
	Cr(II) reactions (includes only those measured by radiolytic methods). Cr_{aq}^{2+}							
5.4	$Cr^{2+} + Br_2^- \rightarrow$ $CrBr^{2+} + Br^-$	$(1.9 \pm 0.2) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by inner sphere diffusion controlled mechanism. $G(CrBr^{2+}) = 2.4$ in γ–radiolysis experiments.	Laur.74–1104
5.5	$Cr^{2+} + Cl_2^- \rightarrow$ $CrCl^{2+} + Cl^-$(a) or $Cr^{3+} + 2Cl^-$(b)	$(2.4 \pm 0.3) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by parallel mechanisms involving inner-sphere (path a) and outer sphere (b) diffusion control with approximately equal probability. $G(CrCl^{2+}) = 1.4$ in γ–radiolysis experiments.	Laur.74–1104
5.6	$Cr^{2+} + I_2^- \rightarrow$ $CrI^{2+} + I^-$	$(1.5 \pm 0.2) \times 10^9$	0.2	22 ± 3	1	pr	Reaction occurs by inner sphere diffusion controlled mechanism. CrI^{2+} characterised by flash photolysis and γ–radiolysis experiments. $G(CrI^{2+}) = 0.85$ at 0°C.	Laur.74–1104
5.7	$Cr^{2+} + MnO_4^-$ (et)	3.7×10^9	$ca.0.01$	20	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Baxe..65–0385
5.8	$Cr^{2+} + N_2O$	$< 10^6$	–	25	nat	γ	Estimated from the values of $G(N_2)$ measured in the γ–radiolysis of $Cr^{3+} + N_2O$ solutions.	Sell72–0844

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
5.9	$Cr^{2+} + O_2 \rightarrow$ CrO_2^{2+}	$(1.6 \pm 0.2) \times 10^8$	–	25 ± 2	2.6–4.3	pr	Measured from the rate of formation of CrO_2^{2+} in the presence of 0.5 mol dm^{-3} 2–methyl–2–propanol. Product characterised by its absorption spectrum and by conductivity measurements.	Sell.76–1134
		$(1.6 \pm 0.2) \times 10^8$	–	RT	1–3	pr	Measured from the rate of formation of CrO_2^{2+}.	Ilan..75–1215
		$(1.9 \pm 0.3) \times 10^8$	–	25 ± 2	3.4	pr (comp)	Measured by competition with 1,4–benzoquinone taking $k(Cr^{2+} + C_6H_4O_2) = 3.2 \times 10^8$ dm^3 mol^{-1} s^{-1}.	Sell.76–1134
5.10	$Cr^{2+} + \cdot CONH_2 \rightarrow$ $CrCONH_2^{2+}$	$(6.5 \pm 0.7) \times 10^8$	–	22 ± 2	0–4.5	pr	Measured by the rate of formation of the product in the presence of 1 mol dm^{-3} formamide. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.11	$Cr^{2+} + \cdot CH_2OH \rightarrow$ $CrCH_2OH^{2+}$	1.6×10^8	–	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.12	$Cr^{2+} + CO_2^- \rightarrow$ $CrCO_2^+$	$(1.1 \pm 0.1) \times 10^9$	ca. 0.04	25 ± 2	1.4	pr	Measured by rate of formation of the product in the presence of 1 mol dm^{-3} formic acid. Product characterised by its spectrum and decay kinetics.	Elli....73–1057
5.13	$Cr^{2+} + \cdot CH_2CHO \rightarrow$ $CrCH_2CHO^{2+}$ or $CrCH_2CH(OH)_2^{2+}$	3.5×10^8	–	22 ± 2	0–1	pr	Measured by the rate of formation of the product, which may be in the form of an acetal.	Cohe.74–1146
5.14	$Cr^{2+} + \cdot CH_2COOH \rightarrow$ $CrCH_2COOH^{2+}$	2.5×10^8	–	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.15	$Cr^{2+} + \cdot CHOH.COOH \rightarrow$ $CrCHOH.COOH^{2+}$	1.4×10^8	–	22 ± 2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146

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TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
5.16	Cr^{2+} + CH$_3$CHOH → CrCH(CH$_3$)OH^{2+}	7.9 x 10^7	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.17	Cr^{2+} + ·CHOHCH$_2$OH → CrCH$_2$CHO^{2+} or CrCH$_2$CH(OH)$_2$$^{2+}$	1.5 x 10^8	–	22±2	3.0–4.5	pr	Measured by the rate of formation of the product. Product is identical to that formed in the reaction Cr^{2+} + CH$_2$CHO (see entry 5.13).	Cohe.74–1146
5.18	Cr^{2+} + ·CH(COOH)$_2$ → CrCH(COOH)$_2$$^{2+}$	6.0 x 10^7	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.19	Cr^{2+} + CH$_3$CHCOOH → CrCH(CH$_3$)COOH^{2+}	1.1 x 10^8	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.20	Cr^{2+} + CH$_3$C(OH)COOH → CrCOH(CH$_3$)COOH^{2+}	9.2 x 10^7	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.21	Cr^{2+} + ·CH$_2$N(CH$_3$)CHO → CrCH$_2$N(CH$_3$)CHO^{2+}	(1.1 ± 0.1) x 10^8	–	22±2	0–4.5	pr	Measured by the rate of formation of the product in the presence of 1 mol dm^{-3} CH$_3$N(CH$_3$)CHO. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.22	Cr^{2+} + (CH$_3$)$_2$COH → CrCOH(CH$_3$)$_2$$^{2+}$	5.1 x 10^7	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.23	Cr^{2+} + ·R → CrR^{2+} ·R = radical from dioxane (H abstraction)	1.0 x 10^8	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.24	Cr^{2+} + ·CH$_2$C(CH$_3$)$_2$OH → CrCH$_2$C(CH$_3$)$_2$OH^{2+}	1.0 x 10^8	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
5.25	Cr^{3+} + CH$_3$CHOCH$_2$CH$_3$ → CrCH(CH$_3$)OCH$_2$CH$_3$$^{2+}$	3.4 x 10^7	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.26	Cr^{2+} + CH$_2$C(CH$_3$)$_2$COOH → CrCH$_2$C(CH$_3$)$_2$COOH^{2+}	1.1 x 10^6	–	22±2	0–1	pr	Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.	Cohe.74–1146
5.27	Cr^{3+} + anthraquinone–2,6–disulphonate → Cr^{3+} + (anthraquinone–2,6–disulphonate)$^-$	(2.8 ± 0.3) x 10^9	–	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl–2–propanol.	Rao.75–1032
5.28	Cr^{3+} + 1,4–benzo–quinone → Cr^{3+} + (1,4–benzoquinone)$^-$	(3.2 ± 0.3) x 10^8	–	25±2	3.4	pr	Measured by the rate of formation of the semiquinone in the presence of 0.5 mol dm^{-3} 2-methyl–2–propanol.	Sell.76–1134
		(3.5 ± 0.4) x 10^9	–	ca.22	7.0	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2-methyl–2–propanol.	Rao.75–1032
5.29	Cr^{2+} + tetra–nitromethane → Cr^{3+} + NO$_2$ + C(NO$_2$)$_3$$^-$	(1.2 ± 0.2) x 10^6	–	25±2	3.4	pr	Measured by the rate of formation of the nitroform anion in the presence of 1 mol dm^{-3} 2-methyl–2–propanol.	Sell.76–1134
	Cr(V) (from CrO$_4$$^{2-}$ + e$_{aq}^-$)							
5.30	Cr^V + Cr^V (dis or af)	$2k/\epsilon_{400}$ = (7 ± 3) x 10^8 cm s^{-1}	0.003	25	nat	pr	–	Sell72–0844

[a] If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

TABLE 6. Copper(I) and copper(III) reactions

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Cu_{aq}^+							
6.1	$Cu^+ + Cu(OH)_2^+$ (et)	$(1.8 \pm 0.6) \times 10^9$	0.003	25	4.8	pr	See comments under entry 6.37.	Sell72–0844
		$(1.6 \pm 0.5) \times 10^9$	0.003	25	6	pr	See comments under entry 6.37.	Sell72–0844
		$(3.6 \pm 1.2) \times 10^9$	0.002	RT	nat	pr	–	Meye71–0174
6.2	$Cu^+ + MnO_4^-$ (et)	5×10^9	ca. 0.08	20	2	pr	Measured by the rate of depletion of the MnO_4^- absorption. Dependence of k on $[Cu^{2+}]$ detected.	Baxe..65–0385
		$(6.4 \pm 0.6) \times 10^9$	0.004	25	nat	pr	Measured by the rate of depletion of the MnO_4^- absorption.	Sell72–0844
6.3	$Cu^+ + N_2O$	$< 10^6$	–	25	nat	γ	Estimated from N_2 yields in the γ–radiolysis of Cu^{2+} + N_2O solutions.	Sell72–0844
6.4	$Cu^+ + \cdot CH_2OH \rightleftharpoons CuCH_2OH^+$	$k_f\ ca.\ 10^{10}$	–	RT	4.5	pr	Identity of product inferred from its absorption spectrum.	Buxt.77–1500
		$k_r\ ca.\ 10^6\ s^{-1}$	–	RT	4.5	pr	Rate constants estimated from rate of growth and decay of $CuCH_2OH^+$.	Buxt.77–1500
6.5	$Cu^+ + (CH_3)_2COH \rightarrow CuCOH(CH_3)_2^+$	$ca.\ 6 \times 10^9$	–	RT	4.5	pr	Identity of product inferred from its absorption spectrum.	Buxt.77–1500
6.6	$CuCOH(CH_3)_2^+ + H^+ \rightarrow Cu^+ +$ products	3.2×10^7	–	RT	3–4.5	pr	Estimated from dependence of decay of absorption attributed to $CuOH(CH_3)_2^+$ on $[H^+]$ (see entry 6.5).	Buxt.77–1500
6.7	$Cu^+ + \cdot CH_2CH_2OH \rightarrow CH_2=CH_2 + OH^- + Cu^{2+}$	1.9×10^{10}	–	RT	4.5	γ	Estimated from yields of Cu^I in γ–radiolysis of Cu^{2+} + C_2H_4 solutions. Products inferred from data for entry 6.8.	Buxt.77–1500
6.8	$Cu^+ + \cdot CH_2(CH_3)_2COH \rightarrow CuCH_2(CH_3)_2COH^+$	2.6×10^9	–	RT	4.5	γ	Product inferred from its absorption spectrum. Estimated from yields of Cu^I in the γ–radiolysis of Cu^{2+} + 2–methyl–2–propanol + C_2H_4 solutions. Final product is $CH_2=C(CH_3)_2$.	Buxt.77–1500
6.9	$Cu^+ +$ acrylamide $\rightleftharpoons$ Cu–acrylamide$^+$	$K = (2.1 \pm 0.1) \times 10^4\ dm^3\ mol^{-1}$ $k_f = 2 \times 10^9$ $k_r = 1.1 \times 10^5\ s^{-1}$	–	25 ± 2	4 2.5 2.5	pr	Measured from the effect of [acrylamide] on the yield and rate of formation of Cu–acrylamide$^+$.	Buxt..76–1186
6.10	$Cu^+ +$ benzoquinone	$< 10^6$	–	25 ± 2	4.9	pr	Estimated from the non–formation of benzosemiquinone in the pulse radiolysis of Cu^{2+} + benzoquinone solutions.	Sell.76–1134

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
6.11	Cu^+ + ethylene $\rightleftharpoons$ Cu–ethylene$^+$	$K = (2.22 \pm 0.1)$ x $10^5\ dm^3\ mol^{-1}$	–	25±2	4	γ	Measured from he effect of admitting ethylene to solutions of Cu–acrylamide$^+$ (see entry 6.9).	Buxt..76–1186
6.12	Cu^+ + fumaric acid $\rightleftharpoons$ Cu–fumaric acid$^+$	$k_f = (1.7 \pm 0.4)$ x 10^9	–	22±2	3.65	pr	Measured from the rate of formation	Meye75–1092
		$k_r = (2.4 \pm 0.4)$ x $10^5\ s^{-1}$ $K = (7.1 \pm 2.0)$ x $10^3\ dm^3\ mol^{-1}$	–	22±2	3.65	pr	of the product in the presence of 1 mol dm^{-3} methanol.	
		$K = (9.0 \pm 2.0)$ x $10^3\ dm^3\ mol^{-1}$	–	22±2	3.65	pr	Measured from the effect of [fumaric acid] on the yield of Cu–fumaric acid$^+$ – in the presence of 1 mol dm^{-3} methanol.	Meye75–1092
6.13	Cu^+ + iso–butene $\rightleftharpoons$ Cu–iso–butene$^+$	$K = (2.7 \pm 0.1)$ x $10^4\ dm^3\ mol^{-1}$	–	25±2	4	γ	Measured from the effect of admitting iso–butene to solutions of Cu–acrylamide$^+$.	Buxt..76–1186
6.14	Cu^+ + maleic acid $\rightleftharpoons$ Cu–maleic acid$^+$	$k_f = (2.0 \pm 0.4)$ x 10^9	–	22±2	3.65	pr	Measured from the rate of formation	Meye75–1092
		$k_r = (1.8 \pm 0.4)$ x $10^5\ s^{-1}$ $K = (1.1 \pm 0.3)$ x $10^4\ dm^3\ mol^{-1}$.	–	22±2	3.65	pr	of the product in the presence of 1 mol dm^{-3} methanol.	
		$K = (1.3 \pm 0.2)$ x $10^4\ dm^3\ mol^{-1}$	–	22±2	3.65	pr	Measured from the effect of [maleic acid] on the yield of Cu–maleic acid$^+$ in the presence of 1 M methanol.	Meye75–1092
6.15	Cu^+ + tetranitro–methane $\rightarrow Cu^{2+}$ + NO_2 + $C(NO_2)_3^-$	(4.2 ± 0.4) x 10^8	–	RT	–	pr	Measured from the rate of formation of the nitroform anion.	Asmu...64–0133
		(4.7 ± 0.5) x 10^8	–	25±2	4.9	pr	Measured from the rate of formation of the nitroform anion.	Sell.76–1134

Cu(I) Complexes
CuL^+ (L = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene)
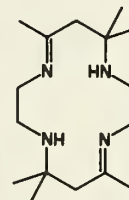
No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
6.16	CuL^+ + Co(bpy)$_3^{3+}$ (et)	(1.2 ± 0.1) x 10^7	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.17	CuL^+ + CoL'(OH$_2$)(OH)$^{2+}$	$< 10^3$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

(L' = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene).

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
6.18	CuL$^+$ + Co(en)$_3$$^{3+}$	$< 10^3$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.19	CuL$^+$ + Co(NH$_3$)$_6$$^{3+}$	$< 10^3$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.20	CuL$^+$ + CoL'(OH)$_2$$^+$	$< 10^3$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
	(L' = 2,3,9,10–tetramethyl–1,4,8,11–tetraazacyclotetradeca–1,3,7,10–tetraene).							
6.21	CuL$^+$ + Cr(bpy)$_3$$^{3+}$ (et)	$(3.7 \pm 0.4) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.22	CuL$^+$ + Fe(bpy)$_3$$^{3+}$	$< 10^3$	0.016–0.028	RT	7.0	pr	Estimated in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.23	CuL$^+$ + H$_3$O$^+$ (pt)	$(5.0 \pm 0.5) \times 10^6$	0.06–0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex.	Tait..76–1039
6.24	CuL$^+$ + H$_2$PO$_4$$^-$	$< 10^4$	0.01–0.1	RT	5.50	pr	–	Tait..76–1039
6.25	CuL$^+$ + N$_2$O (et or O at)	$(1.7 \pm 0.2) \times 10^6$	–	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Reaction possibly involves two electron oxidation to Cu(III) complex.	Tait..76–1039
6.26	CuL$^+$ + O$_2$ → CuLO$_2$$^+$	$(2.6 \pm 0.3) \times 10^7$	–	RT	7.0	pr	Product does not transfer an electron to 1,4–benzoquinone, and identified therefore as O$_2$ adduct.	Tait..76–1039
6.27	CuL$^+$ + Ru(NH$_3$)$_6$$^{3+}$ (et)	$(7.2 \pm 0.7) \times 10^4$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.28	CuL$^+$ + Ru(NH$_3$)$_5$NO^{3+}	$< 10^3$	0.016–0.028	RT	7.0	pr	Estimated in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.29	CuL$^+$ + acetic acid	$< 10^4$	0.015–0.06	RT	4.85	pr	Estimated in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
6.30	CuL$^+$ + 9,10–anthraquinone–2,6–disulphonate (et)	$(4.3 \pm 0.4) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	k/dm³ mol⁻¹ s⁻¹ ª	I	$t/°C$	pH	Method	Comments	Ref.
6.31	CuL⁺ + 9,10–anthra–quinone–2–sulphon–ate (et)	$(1.1 \pm 0.1) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm⁻³ 2–methyl–2–propanol.	Tait..76–1039
6.32	CuL⁺ + 1,4–benzo–quinone (et)	$(2.6 \pm 0.3) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm⁻³ 2–methyl–2–propanol.	Tait..76–1039
6.33	CuL⁺ + 3–benzoyl–pyridine	no reaction observed	0.004	RT	7.0	pr	–	Tait..76–1039
6.34	CuL⁺ + eosin Y	no reaction observed	0.004	RT	7.0	pr	–	Tait..76–1039
6.35	CuL⁺ + fluorescein	no reaction observed	0.004	RT	7.0	pr	–	Tait..76–1039
6.36	CuL⁺ + methyl iodide (et or S_N2)	$(3.1 \pm 0.3) \times 10^6$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm⁻³ 2–methyl–2–propanol.	Tait..76–1039

Cu(III) Reactions
Cu(III) aquo ion ($Cu(OH)_3$, $Cu(OH)_2^+$ and $CuOH^{2+}$)[b]

No.	Reaction	k/dm³ mol⁻¹ s⁻¹ ª	I	$t/°C$	pH	Method	Comments	Ref.
6.37	$CuOH^{2+} \rightleftharpoons Cu(OH)_2^+ + H^+$	$pK = 2.4 \pm 0.2$	var	25	0.6	pr	Degree of hydro–lysis deduced from conductivity experi–ments (see ref. 70–0512). Note: pK of this value is also in keeping with the data of Baxendale *et al* (ref. 65–0394) and of Meyerstein (ref. 71–0174) taking into account equilibrium 6.39.	Sell72–0844
		$pK = 3.05 \pm 0.05$	var	RT	2–7	pr	–	Baxe..65–0394
6.38	$Cu(OH)_2^+ \rightleftharpoons CuOH^+ + OH$	$k_f = (4.2 \pm 1.4) \times 10^4 s^{-1}$ and $K = 1.3 \times 10^{-4}$ dm³ mol⁻¹	var	RT	3.50	pr	Estimated from decay of Cuᴵᴵᴵ in the pre–sence of Br⁻, CH₃OH, H₂O₂ etc. Values of k_r taken to be same as $k(Cu^{2+} + OH)$.	Baxe..65–0394
		$k_f = (2.8 \pm 1.0) \times 10^4 s^{-1}$ and $K = 9.0 \times 10^{-5}$ dm³ mol⁻¹	var	RT	3.65	pr		
6.39	$Cu(OH)_2^+ \rightleftharpoons Cu(OH)_3 + H^+$	$pK > 6$	var	25	0–6	pr	–	Sell72–0844
6.40	$Cu(OH)_2^+ + Cu^+$ (et)	$(1.8 \pm 0.6) \times 10^9$	0.003	25	4.8	pr	Estimated from decay of Cuᴵᴵᴵ in deaerated solutions.	Sell72–0844
		$(1.6 \pm 0.5) \times 10^9$	0.003	25	6	pr	Possibly some contri–bution from $Cu(OH)_3 + Cu^+$.	Sell72–0844
		$(3.6 \pm 1.2) \times 10^9$	0.002	RT	nat	pr	Possibly some con–tribution from $Cu(OH)_3 + Cu^+$.	Meye71–0174
6.41	$Cu(OH)_2^+ + Cu(gly)^+$ (et?)	$(8.1 \pm 0.5) \times 10^7$	0.004	RT	5.5	pr	–	Meye71–0775

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TABLE 6. Copper(I) and copper(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
6.42	$Cu(OH)_2^+ + Cu(OH)_2^+$ (af)	$2k = (4.6 \pm 0.6)$ x 10^7	0.002	RT	6	pr	Estimated from the decay of Cu^{III} in N_2O saturated solutions.	Meye71–0174
		$2k < 5$ x 10^7	0.004	25	6	pr	Possibly some contribution from $Cu(OH)_2^+$ + $Cu(OH)_3$ and $Cu(OH)_3$ + $Cu(OH)_3$.	Sell72–0844
6.43	$Cu(OH)_2^+$ + $CuNO_2^+$ (et)	$ca.$ 3 x 10^9	$ca.$ 0.002	RT	5.2	pr	Estimated from decay of Cu^{III} in presence of NO_2^-.	Meye71–0174
6.44	$Cu(OH)_2^+$ + mena-quinone (?)	(2.0 ± 0.2) x 10^9	–	RT	9.0, 10.6	pr	40% of Cu^{III} claimed to react by electron transfer. Cu^{III} formed by OH + $Cu(ClO_4)_2$.	Rao.73–1047
		–	–	RT	8.0	pr	20.3% electron transfer. Cu^{III} formed by OH + $CuSO_4$.	Rao.73–1047
		–			10.6	pr	39% electron transfer. Cu^{III} formed by OH + $CuSO_4$.	Rao.73–1047

Cu(III) Complexes. (The precise nature of these complexes is uncertain: all were formed by OH oxidation of the corresponding Cu^{II} complex).

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
6.45	$Cu^{III}(NH_3)_n$ + $Cu^{III}(NH_3)_n$ (af?)	$2k = (3.0 \pm 0.5)$ x 10^7	<0.008	RT	11.1	pr	–	Meye71–0775
6.46	$Cu^{III}(\alpha\text{-alanine})_2$ (int et?)	(8.0 ± 2.4) x 10^3 s^{-1}	<0.002	RT	6.3	pr	–	Meye71–0775
6.47	$Cu^{III}(\beta\text{-alanine})_2$ (int et?)	(7.0 ± 2.1) x 10^3 s^{-1}	<0.002	RT	5.8	pr	–	Meye71–0775
6.48	$Cu^{III}(\alpha\text{-amino-n-butyric acid})_2$ (int et?)	(5.0 ± 1.5) x 10^3 s^{-1}	<0.002	RT	6.1	pr	–	Meye71–0775
6.49	$Cu^{III}(\beta\text{-amino-n-butyric acid})_2$ (int et?)	(4.5 ± 1.3) x 10^3 s^{-1}	<0.002	RT	6.0	pr	–	Meye71–0775
6.50	$Cu^{III}(\gamma\text{-amino-n-butyric acid})_2$ (int et?)	(1.2 ± 0.4) x 10^3 s^{-1}	<0.002	RT	4.8	pr	–	Meye71–0775
6.51	$Cu^{III}(\alpha\text{-amino-iso-butyric acid})_2$ (int et?)	(1.5 ± 0.5) x 10^3 s^{-1}	<0.002	RT	6.2	pr	–	Meye71–0775
		(2.5 ± 0.8) x 10^3 s^{-1}	<0.002	RT	7.3	pr	–	Meye71–0775
6.52	$Cu^{III}(en)_n$ (int et?)	$< 3\ s^{-1}$	0.002	RT	5.8	pr	–	Meye71–0775
		$120\ s^{-1}$	0.002	RT	11.6	pr	–	Meye71–0775
6.53	$Cu^{III}(en)_n$ + $Cu^{III}(en)_n$ (af?)	$2k = 5.5$ x 10^5	0.002	RT	5.8	pr	–	Meye71–0775
		$2k = 3.9$ x 10^7	0.002	RT	11.6	pr	–	Meye71–0775
6.54	$Cu^{III}(gly)_2$ (int et?)	(6.0 ± 2.0) x 10^3 s^{-1}	<0.002	RT	6.1	pr	–	Meye71–0775
		(2.2 ± 0.7) x 10^4 s^{-1}	<0.002	RT	7.5	pr	–	Meye71–0775

[a] If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).
[b] The form of Cu^{III} reacting reinterpreted from original references according to equilibria 6.37 and 6.39.

TABLE 7. Europium(II) reactions

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Eu^{2+}_{aq} (Includes only those rate constants measured by pulse radiolysis).							
7.1	$Eu^{2+} + BrO_3^-$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.2	$Eu^{2+} + Co(NH_3)_5Cl^{2+}$	90 ± 9	0.06	25	6	pr	–	Fara.73–0107
	(et–is)	$(4.7 \pm 0.5) \times 10^2$	1.0 (NaClO$_4$)	25	6	pr	–	Fara.73–0107
		$(5.3 \pm 0.5) \times 10^2$	1.0 (NaCl)	25	6	pr	–	Fara.73–0107
7.3	$Eu^{2+} + Co(NH_3)_5CN^{2+}$	< 30	0.06	25	6	pr	–	Fara.73–0107
7.4	$Eu^{2+} + Co(NH_3)_5F^{2+}$	$(2.8 \pm 0.3) \times 10^3$	0.06	25	6	pr	–	Fara.73–0107
	(et–is)	$(1.5 \pm 0.2) \times 10^4$	1.0 (NaClO$_4$)	25	6	pr	–	Fara.73–0107
		$(2.4 \pm 0.2) \times 10^4$	1.0 (NaCl)	25	6	pr	–	Fara.73–0107
7.5	$Eu^{2+} + Co(NH_3)_5OH^{2+}$ (et–is)	ca. 100	0.3	25	–	pr	–	Fara.73–0107
7.6	$Eu^{2+} + Co(NH_3)_5N_3^{2+}$	< 30	0.06	25	6	pr	–	Fara.73–0107
7.7	$Eu^{2+} + Co(NH_3)_5NCS^{2+}$	< 10	0.06	25	6	pr	–	Fara.73–0107
7.8	$Eu^{2+} + Cu^{2+}$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.9	$Eu^{2+} + H_2O_2$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.10	$Eu^{2+} + IO_3^-$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.11	$Eu^{2+} + MnO_4^-$ (et)	6.5×10^9	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.12	$Eu^{2+} + NO_2^-$ (et)	6.2×10^5	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.13	$Eu^{2+} + NO_3^-$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.14	$Eu^{2+} + N_2O$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.15	$Eu^{2+} + O_2$	$< 10^4$	ca. 0.01	RT	nat	pr	–	Fara.72–0065
7.16	$Eu^{2+} + OH$ (et)	9×10^8	–	RT	nat	pr	Measured from the rate of decay of Eu^{2+} in the absence of OH scavengers. Major competing reaction is OH + OH.	Fara.72–0065
		$(1.3 \pm 0.2) \times 10^9$	–	RT	2	pr	–	Pika..73–1084
		3.8×10^9	–	RT	nat	pr	–	Gord65–0799
7.17	$Eu^{2+} + Ru(NH_3)_5Br^{2+}$ (et–is)	ca. 3×10^3	0.06	25	6	pr	–	Fara.73–0107
7.18	$Eu^{2+} + Ru(NH_3)_5Cl^{2+}$ (et–is)	$(1.5 \pm 0.2) \times 10^4$	0.06	25	6	pr	–	Fara.73–0107
7.19	$Eu^{2+} + Ru(NH_3)_5H_2O^{3+}$	$\leq 2 \times 10^3$	0.3	25	2	pr	–	Fara.73–0107
7.20	$Eu^{2+} + Ru(NH_3)_6^{3+}$	ca. 1×10^3	0.06	25	6	pr	–	Fara.73–0107
	(et–is)	$(2.3 \pm 0.2) \times 10^3$	1.0 (NaClO$_4$)	25	6	pr	–	Fara.73–0107
		$(1.5 \pm 0.2) \times 10^4$	1.0 (NaCl)	25	6	pr	–	Fara.73–0107
7.21	$Eu^{2+} + Ru(NH_3)_5OH^{2+}$	$(6.0 \pm 0.6) \times 10^4$	0.06	25	6	pr	–	Fara.73–0107
	(et–is)	$(1.0 \pm 0.1) \times 10^5$	0.3	25	6	pr	–	Fara.73–0107

[a] If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 8. Iron(II) and iron(III) radical complex reactions

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
8.1	$FeH^{2+} + H^+ \rightarrow Fe^{3+} + H_2$	$(1.06 \pm 0.1) \times 10^4$	0.1–1.0	19–24	0.1–1.0	pr	H$_2$ product characterised by vpc; Fe^{3+} by its absorption spectrum.	Jays...69–0434
8.2	$FeHO_2^{2+} \rightarrow Fe^{3+} + HO_2^-$	$(1.8 \pm 0.1) \times 10^3$ s^{-1} $E_a = 8.8 \pm 0.8$ kJ mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	20,25	0.1–0.3	pr	Fe^{III} detected as product.	Jays..73–0038
8.3	$FeHO_2^{2+} + Fe^{2+} \rightleftharpoons FeHO_2Fe^{4+}$	$K = 22 \pm 2$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	20	0.1–0.3	pr	Measured from the effect of [Fe^{II}] on the absorption of FeHO$_2$Fe^{4+}.	Jays..73–0038
		$K = 27 \pm 2$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	25	0.1–0.3	pr		
		$K = 33 \pm 1$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	30	0.1–0.3	pr		
		$K = 37.5$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	40	0.1–0.3	pr		
8.4	$FeHO_2^{2+} + SO_4^{2-} \rightleftharpoons FeHO_2SO_4$	$K = 90 \pm 20$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	22±1	0.1–0.3	pr	Measured from the effect of [SO$_4^{2-}$] on the absorption of FeHO$_2$Fe^{4+}.	Jays..73–1022
8.5	$FeHO_2Fe^{4+} \rightarrow Fe^{3+} + HO_2^- + Fe^{2+}$	$(1.8 \pm 0.1) \times 10^4$ s^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	20	0.1–0.3	pr	Fe^{III} detected as product.	Jays..73–0038
		$(2.5 \pm 0.1) \times 10^4$ s^{-1} $E_a = 47.7 \pm 4.6$ kJ mol^{-1}	1.0 (HClO$_4$/ NaClI$_4$)	25	0.1–0.3	pr		
8.6	$FeHO_2Fe^{4+} + SO_4^{2-} \rightleftharpoons FeHO_2FeSO_4^{2+}$	$K = 100 \pm 20$ dm^3 mol^{-1}	1.0 (HClO$_4$/ NaClO$_4$)	22±1	0.1–0.3	pr	Measured from the effect of [SO$_4^{2-}$] on the absorption of FeHO$_2$Fe^{4+}.	Jays..73–1022
8.7	$FeHO_2SO_4 \rightarrow FeSO_4^+ + HO_2^-$	$ca.$ 10^4 s^{-1}	–	22±1	0.1–0.3	pr	FeSO$_4^+$ characterised by its absorption spectrum.	Jays..73–1022
8.8	$FeHO_2FeSO_4^{2+} \rightarrow FeSO_4Fe^{3+} + HO_2^-$	$ca.$ 10^4 s^{-1}	–	22±1	0.1–0.3	pr	FeSO$_4$Fe^{3+} characterised by its absorption spectrum.	Jays..73–1022

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 9. Mercury(0) and mercury(I) reactions

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Hg^0							
9.1	$Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+}$	$(5.9 \pm 0.6) \times 10^8$	–	RT	3–4	pr	Measured from the pH dependence of the formation of Hg_2^{2+}.	Fuji..73–1080
9.2	$Hg^0 + HgOH^+ \rightarrow$ $Hg_2^{2+} + OH^-$	$(5.0 \pm 0.5) \times 10^8$	–	RT	3–4	pr	Measured from the pH dependence of the formation of Hg_2^{2+}.	Fuji..73–1080
9.3	$Hg^0 + Hg(OH)_2 \rightarrow$ $Hg_2^{2+} + 2OH^-$	$< 5 \times 10^7$	–	RT	3–4	pr	Measured from the pH dependence of the formation of Hg_2^{2+}. See also comments for entry 9.6.	Fuji..73–1080
	Hg_2^+							
9.4	$Hg_2^+ + Hg_2^+$ (et?)	$2k = (1.4 \pm 0.2)$ $\times 10^{10}$	<0.017	RT	1.9	pr	Rate constant calculated taking $\epsilon_{285} = 9000 \text{ dm}^3$ $\text{mol}^{-1} \text{ cm}^{-1}$.	Fara.72–0290
	$Hg(I)$ *Hg_{aq}^+ (and hydrolysed forms)*							
9.5	$Hg^+ \rightleftharpoons HgOH + H^+$	$pK = 5.1$	var	RT	4–7	pr	Measured from the effect of pH on the absorption spectrum of Hg^+.	Fuji...75–1044
9.6	$Hg^+ + Hg^+ \rightarrow Hg^0 + Hg^{2+}$	$2k = (4.9 \pm 0.5)$ $\times 10^9$	→ 0	RT	2.0	pr	Transient product formed, whose decay is dependent on $[Hg^{II}]$, and which gives Hg_2^{2+}. These results taken to indicate that Hg^+ $+ Hg^+$ results in dismutation. Rate constants calculated taking $\epsilon_{255} = 1.4 \times$ $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fuji..73–1080
		$2k = (5.2 \pm 0.5)$ $\times 10^9$	→ 0	RT	4.3	pr		
	$Hg^+ + Hg^+ (\rightarrow Hg_2^{2+})$	$2k = (8.0 \pm 1.0)$ $\times 10^9$	<0.017	RT	1.9	pr	Products not characterised, but reaction considered to involve dimerisation. Rate constant calculated taking $\epsilon_{272} = 7800 \text{ dm}^3$ $\text{mol}^{-1} \text{ cm}^{-1}$.	Fara.72–0290
9.7	$HgOH + HgOH \rightarrow$ $Hg_2O + H_2O$ or $Hg_2(OH)_2$	$2k = (4.4 \pm 0.4)$ $\times 10^9$	< 0.1	RT	–	pr	Products identified from pH dependence of their absorption spectra. Rate constant calculated taking $\epsilon_{260} = 5300 \text{ dm}^3 \text{ mol}^{-1}$ cm^{-1}.	Fuji...75–1044
9.8	$Hg^I + Hg^I$	$2k = (4.9 \pm 1.0)$ $\times 10^9$	–	RT	1.2	pr	–	Pika..75–1218
		$2k = (5.1 \pm 1.0)$ $\times 10^9$	–	RT	3.15	pr	–	Pika..75–1218
		$2k = (3.5 \pm 0.7)$ $\times 10^9$	–	RT	4.8	pr	–	Pika..75–1218
		$2k = ca. 1.1 \times$ 10^{10}	–	RT	10.2	pr	–	Pika..75–1218

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
9.8	$Hg^I + Hg^I$	$2k = ca.\ 1.5\ \text{x}\ 10^{10}$	–	RT	11.0	pr	–	Pika..75–1218
		$2k = (7.0 \pm 1.4)\ \text{x}\ 10^9$	1(KOH)	RT	14	pr	–	Pika..75–1218
			+ data at intermediate pH's					Pika..75–1218
9.9	$Hg^I + O_2$ (et or af)	$(4.0 \pm 0.6)\ \text{x}\ 10^8$	–	RT	2.7	pr	–	Pika..75–1218
		$(1.2 \pm 0.2)\ \text{x}\ 10^9$	–	RT	11.2	pr	–	Pika..75–1218
		$(1.6 \pm 0.2)\ \text{x}\ 10^9$	1(KOH)	RT	14	pr	–	Pika..75–1218

Note: A change in mechanism of the decay of Hg^I aquo ions is observed on increasing the pH. There appears to be no good understanding of why this should be, and we suggest, therefore, that the reaction mechanisms written above should be viewed with caution. Note also that the spectral data for Hg^+ obtained by Faraggi and Amozig (ref. 72–0290) and by Fujita *et al.* (ref. 73–1080) do not correspond.

Hg(I) Complexes
HgBr and related species

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
9.10	$HgBr + HgBr \rightarrow Hg_2Br_2$	$2k = 8\ \text{x}\ 10^9$	–	RT	–	pr	Product characterised by its absorption spectrum.	Jung..76–1042
		$2k = (1.0 \pm 0.1)\ \text{x}\ 10^{10}$	–	RT	–	pr	–	Fuji...76–1087
9.11	$HgBr + O_2 \rightarrow HgBrO_2$	$> 10^9$	–	RT	–	pr	Product characterised by conductivity experiments and non–formation of O_2^-/HO_2 absorption.	Jung..76–1042
9.12	$HgBr + 1,4\text{–benzo–}$ $quinone \rightarrow HgBr^+ +$ $(1,4\text{–benzoquinone})^-$	$> 10^9$	–	RT	5–5.5	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042
9.13	$HgBr + \text{tetranitro–}$ $\text{methane} \rightarrow HgBr^+ +$ $C(NO_2)_3^- + NO_2$	$2.2\ \text{x}\ 10^9$	–	RT	–	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76–1042
9.14	$HgBrO_2 + 1,4\text{–benzo–}$ $quinone \rightarrow HgBr^+ +$ $O_2 + (1,4\text{–benzo–}$ $quinone)^-$	$7\ \text{x}\ 10^8$	–	RT	–	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042

HgCl

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
9.15	$HgCl + HgCl \rightarrow$ Hg_2Cl_2	$2k = (8.0 \pm 0.5)\ \text{x}\ 10^9$	–	RT	–	pr	Product characterised by its absorption spectrum, and gravimetrically giving $G(Hg_2Cl_2) = 3.0$ in solutions containing 2-propanol.	Nazh.73–0043
9.16	$HgCl + O_2 \rightarrow HgClO_2$	$(1.0 \pm 0.3)\ \text{x}\ 10^9$	–	RT	–	pr	Product characterised by conductivity experiments and non–formation of O_2^-/HO_2 absorption.	Nazh.73–0043
9.17	$HgCl + OH \rightarrow$ $HgCl + OH^-$	$ca.\ 10^{10}$	–	RT	–	pr	Products characterised by conductivity experiments.	Nazh.73–0043
9.18	$HgCl + 1,4\text{–benzo–}$ $quinone \rightarrow HgCl^+$ $+ (1,4\text{–benzosemi–}$ $quinone)^-$	$3.0\ \text{x}\ 10^9$	–	RT	–	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042
		$(3.9 \pm 0.4)\ \text{x}\ 10^9$	–	25±2	5.1	pr		Sell.76–1134
9.19	$HgCl + \text{tetranitro–}$ $\text{methane} \rightarrow HgCl^+$ $+ C(NO_2)_3^- + NO_2$	$(4.5 \pm 0.3)\ \text{x}\ 10^9$	–	RT	5–5.5	pr	Nitroform anion product characterised by its absorption spectrum.	Nazh.73–0043

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
9.20	$HgClO_2$ + 1,4–benzo–quinone → $HgCl^+$ + O_2 + (1,4–benzo–semiquinone)$^-$	7×10^9	–	RT	–	pr	Benzosemiquinone product charac–terised by its absorption spectrum.	Jung..76–1042
	HgCN							
9.21	HgCN + HgCN → $Hg_2(CN)_2$	$2k = (3.4 \pm 0.5)$ $\times 10^9$	< 0.2	RT	–	pr	Product charac–terised by its absorption spec–trum and decay to give Hg^0 and $Hg(CN)_2$. Rate constant cal–culated taking ϵ_{285} = 3800 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.	Fuji...75–1203
		$2k = 1.2 \times 10^{10}$	–	RT	–	pr	–	Jung..76–1042
9.22	HgCN + O_2 → $HgCN^+$ + O_2^-	4×10^9	–	RT	–	pr	O_2^- product charac–terised by its absorption spectrum, lifetime in neutral solution, and con–ductivity measure–ments.	Jung..76–1042
9.23	HgCN + OH (et)	3.1×10^9	–	RT	–	pr	Estimated from initial decay of HgCN in the absence of OH scavengers.	Fuji...75–1203
9.24	HgCN + $\cdot CH_2OH$	4.0×10^9	–	RT	–	pr	Estimated from initial decay of HgCN in the presence of methanol.	Fuji...75–1203
9.25	HgCN + CH_3CHOH (et to HgCN?)	3.9×10^9	–	RT	–	pr	Estimated from initial decay of HgCN in the presence of ethanol.	Fuji...75–1203
9.26	HgCN + $(CH_3)_2CHOH$ → Hg^0 + CN^- + CH_3COCH_3 + H^+	2.4×10^9	–	RT	–	pr	Estimated from initial decay of HgCN in the presence of 2–propanol. G(acetone) = 3.0 measured.	Fuji...75–1203
9.27	HgCN + $\cdot CH_2C(CH_3)_2OH$ (af?)	1.6×10^9	–	RT	–	pr	Estimated from initial decay of HgCN in the presence of 2–methyl–2–butanol. Isobutene *not* detected as product.	Fuji...75–1203
9.28	HgCN + 1,4–benzo–quinone → $HgCN^+$ + (1,4–benzoquinone)$^-$	3.5×10^9	–	RT	–	pr	Benzosemiquinone product charac–terised by its absorption spectrum.	Jung..76–1042
9.29	HgCN + tetranitro–methane → $HgCN^+$ + $C(NO_2)_3^-$ + NO_2	3.1×10^9	–	RT	–	pr	Nitroform anion product charac–terised by its absorption spectrum.	Jung..76–1042
	HgI							
9.30	HgI + HgI → Hg_2I_2	$2k = 5.0 \times 10^9$	–	RT	–	pr	Product charac–terised by its absorption spectrum.	Jung..76–1042

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
9.31	HgI + $O_2 \rightarrow$ HgIO$_2$	$> 10^9$	–	RT	–	pr	Product characterised by conductivity experiments and nonformation of O_2^-/HO_2 absorption.	Jung..76–1042
9.32	HgI + 1,4–benzoquinone $\rightarrow$ HgI$^+$ + (1,4–benzoquinone)$^-$	$> 10^9$	–	RT	–	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042
9.33	HgI + tetranitromethane $\rightarrow$ HgI$^+$ + C(NO$_2$)$_3^-$ + NO$_2$	1.4×10^9	–	RT	–	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76–1042
	HgSCN							
9.34	HgSCN + HgSCN $\rightarrow$ Hg$_2$(SCN)$_2$	$2k = 6.0 \times 10^9$	–	RT	–	pr	Product characterised by its absorption spectrum.	Jung..76–1042
9.35	HgSCN + $O_2 \rightarrow$ HgSCNO$_2$	$> 10^9$	–	RT	–	pr	Product characterised by conductivity experiments and nonformation of O_2^-/HO_2 absorption.	Jung..76–1042
9.36	HgSCN + 1,4–benzoquinone $\rightarrow$ HgSCN$^+$ + (1,4–benzoquinone)$^-$	$> 10^9$	–	RT	–	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042
9.37	HgSCN + tetranitromethane $\rightarrow$ HgSCN$^+$ + C(NO$_2$)$_3^-$ + NO$_2$	2.8×10^9	–	RT	–	pr	Nitroform anion product characterised by its absorption spectrum.	Jung..76–1042
9.38	HgSCNO$_2$ + 1,4–benzoquinone $\rightarrow$ HgSCN$^+$ + O_2 + (1,4–benzoquinone)$^-$	1.0×10^9	–	RT	–	pr	Benzosemiquinone product characterised by its absorption spectrum.	Jung..76–1042

[a]If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

TABLE 10. Indium(II) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	In^{2+}_{aq}							
10.1	$In^{2+} + In^{2+}$ (et or af)	$2k = ca.\ 1.2\ \times\ 10^9$	0.7 (LiClO$_4$)	RT	3	pr	Reinterpreted from data in ref. 76–1087.	Tayl.69–0971
		$2k = (1.6 \pm 0.2)\ \times 10^9$	0.0075	25	3.6	pr	Measured in the pre- sence of 1 mol/dm^3 2–methyl–2–propanol taking $\epsilon_{250} = 7000$ dm^3 mol^{-1} cm^{-1}.	R.M. Sellers, unpub. data
10.2	$In^{2+} + OH$ (et)	$2k = (4.9 \pm 0.7)\ \times 10^9$	–	25	3.6	pr	Measured from the initial decay of In^{2+} in the absence of OH scavengers.	R.M. Sellers, unpub. data
10.3	$In^{2+} + N_2O$	$< 10^6$	–	25	nat	γ	Estimated from the values of $G(N_2)$ measured in the γ–radiolysis of $In^{3+} + N_2O$ solutions.	Sell72–0844

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 11. Iridium(II) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Ir^{II} (from $e^-_{aq} + IrCl_6^{3-}$)							
11.1	$Ir^{II} + Ir^{II}$ (dis)	$2k = (3.3 \pm 0.4)\ \times 10^9$	0.0018	RT	–	pr	–	Bros73–1066

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 12. Manganese(I) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Mn^+_{aq}							
12.1	$Mn^+ + Cu^{2+}$ (et?)	$k_{rel} = 1.6 \pm 0.2$	2.0 (MnSO$_4$)	RT	5–8	γ	Measured by competi- tion kinetics using NO$_3^-$ as competitor in the presence of 0.5 mol dm^{-3} MnSO$_4$. Rate constant relative to $k(Mn^+ + NO_3^-)$.	Fiti70–0117
12.2	$Mn^+ + IO_3^-$ (et?)	$k_{rel} = 1.4 \pm 0.1$	2.0 (MnSO$_4$)	RT	5–8	γ	Measured by competi- tion kinetics using NO$_3^-$ as competitor in the presence of 0.5 mol dm^{-3} MnSO$_4$. Rate constant relative to $k(Mn^+ + NO_3^-)$.	Fiti70–0117
12.3	$Mn^+ + NO_3^-$ (et?)	see entries 12.1 and 12.2.						

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for $2k$).

TABLE 13. Molybdenum reactions

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	$[Mo_2(O_2CCF_3)_4]^-$ *(from $Mo_2(O_2CCF_3)_4 + e_s^-$ in methanol)*							
13.1	$[Mo_2(O_2CCF_3)_4]^- +$ $[Mo_2(O_2CCF_3)_4]^-$ (dis?)	$'k' = (4.5 \pm 1.0)$ x 10^9	–	RT	–	pr	Measured from decay of Mo(1 1/2) species in methanol. Two decay processes observed, one of which believed to be a dismutation reaction. Rate constant (unclear whether k or $2k$) calculated taking $\epsilon_{780} = 2600$ dm³ mol⁻¹ cm⁻¹. Note that if the slower process does not involve the Mo(1 1/2) species, the value of ϵ, and hence k, is incorrect.	Baxe...76–1003
		$'k' = (2.5 \pm 1.0)$ x 10^8	–	RT	–	pr		
13.2	$[Mo_2(O_2CCF_3)_4]^-$ $+ O_2$ (af?)	(5.9 ± 0.3) x 10^9	–	RT	–	pr	Measured in Methanol. Starting material $[Mo_2(O_2CCF_3)_4]$ not regenerated, so reaction does not involve electron transfer.	Baxe...76–1003

[a]If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for $2k$).

TABLE 14. Nickel(I) and nickel(III) reactions

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.1	$Ni^+ + BrO_3^-$	$< 8.4 \times 10^6$	0.08	RT	nat	pr	–	Meye.68–0855
14.2	$Ni^+ + Cd^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
14.3	$Ni^+ + Co(en)_3^{3+}$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.4	$Ni^+ + cis-$ Co(en)₂Cl₂⁺ (et)	$(5.9 \pm 0.9) \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.5	$Ni^+ + trans-$ Co(en)₂Cl₂⁺ (et)	$(8.3 \pm 2.1) \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.6	$Ni^+ + Co(en)_2CO_3^+$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.7	$Ni^+ + cis-Co(en)_2F_2^+$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.8	$Ni^+ + Co(en)_2FH_2O^{2+}$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.9	$Ni^+ + cis-$ Co(en)₂NH₃Cl²⁺ (et)	$(4.7 \pm 0.7) \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.10	$Ni^+ + cis-$ Co(en)₂NH₃NO₂²⁺ (et)	$(3.3 \pm 0.8) \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.11	$Ni^+ + Co(NH_3)_6^{3+}$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.12	$Ni^+ + Co(NH_3)_5Br^{2+}$ (et)	$(1.05 \pm 0.2) \times 10^9$	0.08	RT	4.0	pr	–	Meye.69–0428
14.13	$Ni^+ + Co(NH_3)_5Cl^{2+}$ (et)	$(6.5 \pm 1.0) \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.14	$Ni^+ + Co(NH_3)_5CN^{2+}$ (et)	$(3.3 \pm 0.8) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
14.15	$Ni^+ + Co(NH_3)_5F^{2+}$	$< 5 \times 10^6$	0.08	RT	5–6	pr	–	Meye.69–0428
14.16	$Ni^+ + Co(NH_3)_5H_2O^{3+}$	$< 5 \times 10^6$	0.08	RT	4.0	pr	–	Meye.69–0428
14.17	$Ni^+ + Co(NH_3)_5OH^{2+}$(et)	$(1.3 \pm 0.3) \times 10^6$	0.08	RT	7.6	pr	–	Meye.69–0428
14.18	$Ni^+ + Co(NH_3)_5N_3^{2+}$(et)	$(5.8 \pm 1.5) \times 10^8$	0.08	RT	7.6	pr	–	Meye.69–0428
14.19	$Ni^+ +$ Co(NH₃)₅NCS²⁺ (et)	$(4.1 \pm 1.0) \times 10^6$	0.08	RT	7.6	pr	–	Meye.69–0428
14.20	$Ni^+ +$ Co(NH₃)₅OOCCH₃²⁺	$< 5 \times 10^6$	0.08	RT	5.6	pr	–	Meye.69–0428
14.21	$Ni^+ + Cr^{3+}$	$< 10^7$	–	RT	nat	pr	–	Baxe.66–0848
14.22	$Ni^+ + Cu^{2+}$	$< 2.4 \times 10^7$	0.08	RT	nat	pr	–	Meye.68–0855
14.23	$Ni^+ + H_2O_2 \longrightarrow$ Ni²⁺ + OH + OH⁻	$(3.2 \pm 0.3) \times 10^7$	–	25	nat	pr	–	Buxt..76–1072
		$(4.3 \pm 0.6) \times 10^7$	–	RT	nat	pr	–	Meye.68–0855
		2.1×10^8	–	RT	nat	pr	Products identified in γ–radiolysis studies (see ref. 73–0039).	Buxt..67–0062
14.24	$Ni^+ + H_3O^+$	$< 10^6$	0.08	RT	nat	pr	–	Meye.68–0855
14.25	$Ni^+ + IO_3^-$ (et)	$(2.2 \pm 0.3) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
14.26	$Ni^+ + MnO_4^-$ (et)	7.5×10^9	0.005	RT	nat	pr	Measured by the rate of depletion of the MnO₄⁻ absorption.	Baxe..65–0385
14.27	$Ni^+ + Ni^+$	slow ($< 10^8$)	var	RT	nat	pr	Estimated from decay of Ni⁺ in presence and absence of OH scavengers.	Kelm..74–1037
14.28	$Ni^+ + NO_2^-$ (et)	$(1.5 \pm 0.2) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
14.29	$Ni^+ + NO_3^-$	$< 1.4 \times 10^6$	0.08	RT	nat	pr	–	Meye.68–0855
14.30	$Ni^+ + N_2O \rightarrow$ NiO⁺ + N₂	6.3×10^6	–	RT	nat	pr	Measured in the presence of 1 mol dm⁻³ NiSO₄	Meye.68–0855
		$(9.1 \pm 0.9) \times 10^6$	–	25 ± 2	nat	pr	Measured in the presence of 0.5 mol dm⁻³ NiSO₄.	Buxt..76–1072
		5.1×10^7	–	RT	nat	pr	–	Buxt..67–0062
		$E_a = 40.6 \pm 3.8$ kJ mol⁻¹	–	1–30	nat	pr	Products inferred from γ–ray induced chain reaction in the system Ni²⁺ + HCO₂⁻ + N₂O. $G(N_2)$ also measured in Ni²⁺ + N₂O solutions. (see ref. 73–0039).	Buxt..67–0062

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/^\circ\mathrm{C}$	pH	Method	Comments	Ref.
14.31	$Ni^+ + OH \rightarrow$ $Ni^{2+} + OH^-$	2×10^{10}	–	RT	nat	pr	Measured from a computer fit of the decay of Ni^+ in the absence of OH scavengers assuming competing reactions to be OH + OH and Ni^+ + H_2O_2. Product identified by conductivity measurements (but see ref. 75–1027).	Kelm...74–1037
14.32	$Ni^+ + O_2 \rightarrow NiO_2^+$	$(1.4 \pm 0.2) \times 10^9$	–	RT	nat	pr	–	Meye.68–0855
		2.2×10^9	–	RT	nat	pr	–	Baxe..66–0848
							Product characterised by its absorption spectrum (ref. 76–1072), reactivity with tetranitromethane and lack of reactivity with 1,4–benzoquinone (ref. 76–1134).	
14.33	$Ni^+ + Pb^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
14.34	$Ni^+ + Ru(NH_3)_6^{3+}$ (et)	$(4.0 \pm 0.6) \times 10^8$	0.08	RT	nat	pr	–	Navo.70–1229
14.35	$Ni^+ + S_2O_8^{2-} \rightarrow$ $Ni^{2+} + SO_4^- + SO_4^{2-}$	$(1.5 \pm 0.2) \times 10^8$	0.049	25 ± 2	nat	pr	SO_4^- product characterised by its absorption spectrum and decay kinetics.	Tait..76–1001
14.36	$Ni^+ + Zn^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
14.37	$Ni^+ + \cdot CH_2OH \rightarrow$ $NiCH_2OH^+$	4.2×10^9	–	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74–1037
14.38	$Ni^+ + CO_2^- \rightarrow NiCO_2$	6.6×10^9	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74–1037
14.39	$Ni^+ + \cdot C_2H_4OH \rightarrow$ $NiC_2H_4OH^+$	2.3×10^9	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74–1037
14.40	$Ni^+ + CH_3COHCH_3 \rightarrow$ $NiCOH(CH_3)_2$	1.4×10^9	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74–1037
14.41	$Ni^+ + H_2C(CH_3)_2OH \rightarrow$ $Ni^{2+} + OH^- + CH_2=C(CH_3)_2$	3×10^9	4×10^{-4}	RT	nat	pr	Isobutene detected as product; OH^- detected by conductivity measurements.	Kelm...74–1037
14.42	$Ni^+ + \cdot C_5H_9 \rightarrow NiC_5H_9^+$ ($\cdot C_5H_9$ = cyclopentyl radical)	2.8×10^9	4×10^{-4}	RT	nat	pr	Product characterised by its absorption spectrum and conductivity measurements.	Kelm...74–1037

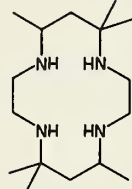TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.43	$Ni^+ + $ allyl alcohol $\rightarrow$ Ni–allyl alcohol$^+$	ca. 10^8	–	25 ± 2	nat	pr	–	Buxt..76–1072
14.44	$Ni^+ + $ 1,4–benzo–quinone $\rightarrow Ni^{2+} + $ (1,4–benzoquinone)$^-$	$(2.3 \pm 0.5) \times 10^8$	–	25	6.0	pr	Measured by the rate of formation of the semiquinone in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Sell.76–1134
14.45	$Ni^+ + $ menaquinone $\rightarrow Ni^{2+} + $ (menaquinone)$^-$	2.4×10^9 $(2.5 \pm 0.3) \times 10^9$	– –	ca. 25 RT	7.0 7.0	pr pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm^{-3} 2–methyl–2–propanol.	Rao.75–1032 Rao.73–1047
14.46	$Ni^+ + $ tetranitro–methane $\rightarrow Ni^{2+} + $ C(NO$_2$)$_3^- + $ NO$_2$	$(1.4 \pm 0.2) \times 10^9$	–	25 ± 2	5.9	pr	Measured by the rate of formation of the nitroform anion in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Sell.76–1134

Ni(I) Complexes
Ni^I–cyano complexes

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.47	$Ni(CN)_3^{2-} + Ni(CN)_3^{2-} \rightarrow Ni_2(CN)_6^{4-}$	$2k = (1.5 \pm 0.2) \times 10^8$	0.1 (HCO$_2$Na)	20 ± 2	–	pr	Product charac–terised by its absorption spectrum.	Mula....74–1072
14.48	$Ni(CN)_4^{3-} \rightarrow Ni(CN)_3^{2-} + CN^-$	$(8.1 \pm 1.0) \times 10^3$ s^{-1}	0.1 (HCO$_2$Na)	20 ± 2	–	pr	Ni(CN)$_3^{2-}$ charac–terised by its absorption spectrum.	Mula....74–1072

NiL$^+$ (L = 5,5,7,12,12,14–hexamethyl–1,4,8,11–tetraazacyclotetradecane).

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.49	$NiL^+ + Co(bpy)_3^{3+}$	$(1.3 \pm 0.1) \times 10^9$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.50	$NiL^+ + CoL'(OH_2)(OH)^{2+}$ (et)	$(1.1 \pm 0.1) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

(L' = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene).

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.51	$NiL^+ + Co(en)_3^{3+}$ (et)	$(1.1 \pm 0.1) \times 10^5$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.52	$NiL^+ + Co(NH_3)_6^{3+}$ (et)	$(1.9 \pm 0.2) \times 10^5$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.53	$NiL^+ + CoL'(OH)_2^+$ (et)	$(1.7 \pm 0.2) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

(L' = 2,3,9,10–tetramethyl–1,4,8,11–tetraazacyclotetradeca–1,3,8,10–tetraene).

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.54	$NiL^+ + Cr(bpy)_3{}^{3+}$ (et)	$(7.7 \pm 0.8) \times 10^8$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.55	$NiL^+ + Fe(bpy)_3{}^{3+}$ (et)	$(6.4 \pm 0.6) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.56	$NiL^+ + H_3O^+$ (pt)	$(1.1 \pm 0.1) \times 10^6$	0.06–0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex.	Tait..76–1039
14.57	$NiL^+ + H_2PO_4{}^-$ (pt)	$< 10^4$	0.01–0.1	RT	5.50	pr	–	Tait..76–1039
14.58	$NiL^+ + N_2O$ (et or O at)	$(3.9 \pm 0.4) \times 10^7$	–	RT	7.0	pr	Reaction possibly involves two electron oxidation to Ni(III) complex.	Tait..76–1039
14.59	$NiL^+ + O_2 \rightarrow$ $NiL^{2+} + O_2{}^-$	$(1.6 \pm 0.2) \times 10^9$	–	RT	7.0	pr	Product transfers an electron to 1,4–benzoquinone but not menaquinone, and identified therefore as $O_2{}^-$, although O_2 adduct, $NiLO_2{}^+$ could conceivably react in same way.	Tait..76–1039
14.60	$NiL^+ + Ru(NH_3)_6{}^{3+}$ (et)	$(3.8 \pm 0.4) \times 10^8$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.61	$NiL^+ + Ru(NH_3)_5NO^{3+}$ (et)	$(7.4 \pm 0.7) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.62	$NiL^+ + $ acetic acid (pt)	$(1.2 \pm 0.1) \times 10^4$	0.015–0.06	RT	4.85	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.63	$NiL^+ + $ 9,10–anthraquinone–2,6–disulphonate (et)	$(4.8 \pm 0.5) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.64	$NiL^+ + $ 1,4–benzoquinone (et)	$(4.8 \pm 0.5) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.65	$NiL^+ + $ 3–benzoylpyridine (et)	$(2.5 \pm 0.3) \times 10^8$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.66	$NiL^+ + $ fluorescein (et)	$(3.2 \pm 0.3) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039
14.67	$NiL^+ + $ methyl iodide (et or S_N2)	$(4.6 \pm 0.5) \times 10^8$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Tait..76–1039

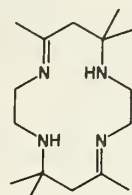TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.

NiL^+ ($L = 5,7,7,12,14,14$–hexamethyl–$1,4,8,11$–tetraazacyclotetradeca–$4,11$–diene).

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.68	$NiL^+ + Co(bpy)_3^{3+}$ (et)	$(1.3 \pm 0.1) \times 10^9$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.69	$NiL^+ + CoL'(OH_2)(OH)^{2+}$ (et)	$(2.6 \pm 0.3) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

(L' = 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclotetradeca–4,11–diene).

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.70	$NiL^+ + Co(en)_3^{3+}$ (et)	$(1.1 \pm 0.1) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.71	$NiL^+ + Co(NH_3)_6^{3+}$ (et)	$(1.9 \pm 0.2) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.72	$NiL^+ + CoL'(OH)_2^+$ (et)	$(3.6 \pm 0.4) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039

(L' = 2,3,9,10–tetramethyl–1,4,8,11–tetraazacyclotetradeca–1,3,8,10–tetraene).

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.73	$NiL^+ + Cr(bpy)_3^{3+}$	$(1.1 \pm 0.1) \times 10^8$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.74	$NiL^+ + Fe(bpy)_3^{3+}$ (et)	$(2.2 \pm 0.2) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.75	$NiL^+ + H_3O^+$ (pt)	$(1.3 \pm 0.1) \times 10^6$	0.06–0.3	RT	<1.25	pr	Reaction may involve proton transfer to the metal centre to give a hydrido complex	Tait..76–1039
14.76	$NiL^+ + H_2PO_4^-$ (pt)	$(2.4 \pm 0.2) \times 10^5$	0.01–0.1	RT	5.50	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.77	$NiL^+ + N_2O$ (et or O at)	$(1.8 \pm 0.2) \times 10^7$	–	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol. Reaction possibly involves two electron oxidation to Ni^{III} complex.	Tait..76–1039
14.78	$NiL^+ + O_2 \rightarrow NiL^{2+} + O_2^-$	$(1.7 \pm 0.2) \times 10^9$	–	RT	7.0	pr	Product transfers an electron to 1,4–benzoquinone but not menaquinone, and identified therefore as O_2^-, although O_2 adduct $NiLO_2^+$, could conceivably react in same way.	Tait..76–1039

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TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
14.79	$NiL^+ + Ru(NH_3)_6^{3+}$ (et)	$(4.5 \pm 0.5) \times 10^6$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.80	$NiL^+ + Ru(NH_3)_5NO^{3+}$ (et)	$(3.5 \pm 0.4) \times 10^7$	0.016–0.028	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.81	$NiL^+ + $ acetic acid (pt)	$(1.9 \pm 0.2) \times 10^5$	0.015–0.06	RT	4.85	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.82	$NiL^+ + $ 9,10–anthra–quinone–2,6–disulphonate (et)	$(5.0 \pm 0.5) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.83	$NiL^+ + $ 1,4–benzoquinone (et)	$(3.8 \pm 0.4) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.84	$NiL^+ + $ 3–benzoylpyri–dine (et)	$(7.5 \pm 0.8) \times 10^6$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.85	$NiL^+ + $ eosin Y (et)	$(2.7 \pm 0.3) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.86	$NiL^+ + $ fluorescein (et)	$(3.3 \pm 0.3) \times 10^9$	0.004	RT	7.0	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
14.87	$NiL^+ + $ methyl iodide (et or S_N2)	$(1.3 \pm 0.1) \times 10^6$	0.01	RT	9.2	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2–propanol.	Tait..76–1039
	Ni(I) radical complexes							
14.88	$NiCH_2OH^+ + H_2O \rightarrow Ni^{2+} + CH_3OH + OH^-$	$7\ \text{s}^{-1}$	–	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74–1037
14.89	$NiCH_2OH^+ + H_2O_2$ (et?)	7.3×10^3	–	RT	nat	pr	–	Kelm...74–1037
14.90	$NiCO_2 + H_2O$	$< 1\ \text{s}^{-1}$	–	RT	nat	pr	–	Kelm...74–1037
14.91	$NiC_2H_4OH^+ + H_2O \rightarrow Ni^{2+} + C_2H_5OH + OH^-$	$5\ \text{s}^{-1}$	–	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74–1037
14.92	$NiC_2H_4OH^+ + H_2O_2$ (et?)	2.3×10^4	–	RT	nat	pr	–	Kelm...74–1037
14.93	$NiCOH(CH_3)_2^+ + H_2O$	$< 1\ \text{s}^{-1}$	–	RT	nat	pr	–	Kelm...74–1037
14.94	$NiCOH(CH_3)_2^+ + H_2O_2$	1.1×10^6	–	RT	nat	pr	–	Kelm...74–1037
14.95	$NiC_2H_4OC_2H_5^+ + H_2O$	$< 1\ \text{s}^{-1}$	–	RT	nat	pr	–	Kelm...74–1037
14.96	$NiC_2H_4OC_2H_5^+ + H_2O_2$	1.3×10^3	–	RT	nat	pr	–	Kelm...74–1037
14.97	$NiC_5H_9^+ + H_2O \rightarrow Ni^{2+} + C_5H_{10} + OH^-$	$49\ \text{s}^{-1}$	–	RT	nat	pr	Products characterised by conductivity experiments.	Kelm...74–1037
14.98	$NiC_5H_9^+ + H_2O_2$ (C_5H_9 = cyclopentyl radical)	$< 5 \times 10^5$	–	RT	nat	pr	–	Kelm...74–1037
	$NiO_2^+ NiO_2H^{2+}$							
14.99	$NiO_2^+ \rightarrow Ni^{2+} + O_2^-$	$780 \pm 80\ \text{s}^{-1}$	–	25 ± 2	5.7	pr	Measured from the rate of formation of the nitroform anion in solutions contining tetra-nitromethane and 1 mol dm^{-3} 2–methyl–2–propanol.	Sell.76–1134

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/^\circ\mathrm{C}$	pH	Method	Comments	Ref.
14.100	$NiO_2^+ + H^+ \rightleftharpoons$ NiO_2H^{2+}	$K = 2000 \pm 1200\ \mathrm{M^{-1}}$ (i.e. $pK_a = 3.2 \pm 0.3$)	0.04	25 ± 2	3.0–5.7	pr	Measured from the pH dependence of the rate of formation of the nitroform anion in solutions containing tetranitromethane and $1\ \mathrm{mol\ dm^{-3}}$ 2–methyl–2–propanol.	Sell.76–1134
14.101	$NiO_2H^{2+} \rightarrow$ $Ni^{2+} + HO_2$	$> 2800\ \mathrm{s^{-1}}$	–	25 ± 2	3.0	pr	Estimated from the rate of formation of the nitroform anion in solutions containing tetra-nitromethane and 1 $\mathrm{mol\ dm^{-3}}$ 2–methyl–2–propanol.	Sell.76–1134
	Ni(III) complexes							
14.102	$Ni^{III}(NH_3)_n + N_2H_4$	$(4 \pm 1) \times 10^6$	–	RT	11.3	pr	–	Lati.72–0460
14.103	$Ni^{III}(NH_3)_n + Ni^{III}(NH_3)_n$	$2k < 3.5 \times 10^7$	–	RT	11.3	pr	–	Lati.72–0460

Rate constants for the decay of $Ni^{III}(en)_n$ and $Ni^{III}(gly)_n$ are given in tables III and IV respectively of ref. 72–0461. These rate constants cannot be attributed to any specific reaction.

[a] If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

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TABLE 15. Lead(I) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Pb^+_{aq}							
15.1	$Pb^+ + Cd^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
15.2	$Pb^+ + Cr^{3+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
15.3	$Pb^+ + Ni^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
15.4	$Pb^+ + O_2 \rightarrow$ $Pb^{2+} + O_2^-$	3.9×10^9	–	RT	nat	pr	Product transfers an electron to 1,4–benzoquinone and tentatively identified as O_2^-. (Ref. 76–1134).	Baxe..66–0848
15.5	$Pb^+ + OH$ (et)	7.7×10^8	–	RT	nat	pr	Reinterpreted from data in ref. 66–0848 on decay of Pb^+ in the absence of OH scavengers. Principal competing reaction, $Pb^+ + Pb^+$, not taken into account.	Baxe..66–0848
15.6	$Pb^+ + Zn^{2+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
15.7	$Pb^I + $ 1,4–benzo–quinone $\rightarrow Pb^{2+} +$ (1,4–benzoquinone)$^-$	$(4.1 \pm 0.8) \times 10^9$	–	25 ± 2	6.3	pr	Lead(II) acetate salt used, Pb^+ may be complexed to acetate. Measured from the rate of formation of the benzosemiquinone product in the presence of 1 mol $\mathrm{dm^{-3}}$ 2–methyl–2–propanol.	Sell.76–1134
15.8	$Pb^+ + $ menaquinone $\rightarrow$ $Pb^{2+} +$ (menaquinone)$^-$	$(3.7 \pm 0.4) \times 10^9$	–	RT	7.2	pr	Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol $\mathrm{dm^{-3}}$ 2–methyl–2–propanol.	Rao.75–1032 Rao.73–1047

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 16. Praseodymium(IV) reactions

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
16.1	$Pr^{4+} + H_2O \rightleftharpoons$ $PrOH^{3+} + H^+$	$K = (7 \pm 1) \times 10^{-4}$ or $pK_a = 3.1 \pm 0.1$	var	RT	1.95–5.87	pr	Measured from effect of pH on absorption of Pr(IV).	Fara.72–0066
16.2	$Pr^{IV} + Br^-$ (et or af)	$(1.2 \pm 0.4) \times 10^{10}$	0.75 $[Pr_2(SO_4)_3]$	RT	nat	pr	–	Fara.72–0066
16.3	$Pr^{IV} + H_2O_2$ (H at ?)	$(8 \pm 1) \times 10^6$	0.75 $[Pr_2(SO_4)_3]$	RT	nat	pr	–	Fara.72–0066
16.4	$Pr^{IV} + HSO_4^-$ (et or H at)	$(2.0 \pm 0.3) \times 10^6$	–	RT	2–3.8	pr	–	Fara.72–0066
16.5	$Pr^{IV} + NO_2^-$ (et?)	$(3 \pm 1) \times 10^7$	0.75 $[Pr_2(SO_4)_3]$	RT	nat	pr	–	Fara.72–0066
16.6	$Pr^{IV} + Pr^{IV}$ (see comments)	$2k = (1.6 \pm 0.8) \times 10^8$	–	RT	5.8	pr	Stable products of reaction suggested to be Pr^{III} and O_2. Initial product possibly an oxo or hydroxo bridged dipraseodymium species.	Fara.72–0066

[a] If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 17. Platinum(I) and platinum(III) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Pt^I Reactions							
	Pt^I from $PtCl_4{}^{2-}$ + e_{aq}^-							
17.1	Pt^I + N_2O (et or O at)	$\leqslant 4 \times 10^6$	–	RT	nat	pr	–	Ghos.69–0144
17.2	Pt^I + O_2 (et or af)	$\leqslant 2 \times 10^7$	–	RT	nat	pr	–	Ghos.69–0144
17.3	Pt^I + $Pt^I \rightarrow Pt^0$ + Pt^{II}	$'k' = (4.1 \pm 0.5)$ $\times 10^9$	0.003	RT	nat	pr	Unclear whether rate constants refer to k or $2k$.	Ghos.69–0144
		$'k' = (3.15 \pm 0.15)$ $\times 10^9$	0.013	RT	nat	pr	Measured in the presence of 0.1 mol $\mathrm{dm^{-3}}$ KCl.	Ghos.69–0144
		$'k' = ca.\ 2.5\ \times$ $\times 10^9$	0.018	RT	2	pr	–	Ghos.69–0144
							Products identified in γ–radiolysis experiments (see ref. 62–0164).	
	Pt^I from $Pt(CN)_4{}^{2-}$ + e_{aq}^-							
17.4	Pt^I + N_2O (et or O at)	$(1.8 \pm 0.25) \times 10^7$	–	RT	nat	pr	–	Ghos.69–0144
17.5	Pt^I + O_2 (et or af)	$(3.5 \pm 0.5) \times 10^9$	–	RT	nat	pr	–	Ghos.69–0144
	Pt^I from $PtLCl^+$ + e_{aq}^- (L = diethylenetriamine).							
17.6	Pt^I + Pt^I (? see comments)	$2k = (4.6 \pm 2.0)$ $\times 10^7$	2×10^{-4}	ca. 25	nat	pr	Rate constant represents decay of second transient produced from Pt^{II} + e_{aq}^-. First transient decays by a first order reaction with $(2.3 \pm 1.3) \times 10^5$ $\mathrm{s^{-1}}$, probably associated with the substitution of Cl^- by H_2O.	Stor...75–1188
	Pt^I from $PtLCl^+$ + H (L = diethylenetriamine).							
17.7	Pt^I + Pt^I (dis?)	$2k = (6.8 \pm 0.8)$ $\times 10^9$	–	ca. 25	2–3	pr	–	Stor...75–1188
	Pt^I from $Pt(en)_2{}^{2+}$ + e_{aq}^-							
17.8	Pt^I + Pt^I (dis?)	$2k = (9.0 \pm 0.8)$ $\times 10^8$	4×10^{-4}	ca. 25	nat	pr	–	Stor...75–1188
	Pt^I (from $Pt(en)_2{}^{2+}$ + H							
17.9	Pt^I + Pt^I (dis?)	$2k = (2.8 \pm 0.6)$ $\times 10^8$	–	ca. 25	2–3	pr	–	Stor...75–1188
	Pt^I from $PtLCl^+$ + H (L = tetraethyldiethylenetriamine).							
17.10	Pt^I + Pt^I (dis?)	$2k = (1.3 \pm 0.6)$ $\times 10^{11}$ (!)	–	ca.	2–3	pr	–	Stor...75–1188
	Pt^{III} Reactions							
	Pt^{III} from $PtCl_4{}^{2-}$ + $Cl_2{}^-$							
17.11	$(Pt^{III})^i \rightarrow (Pt^{III})^{ii}$ (see comments for mechanism)	$(3 \pm 1) \times 10^5\ \mathrm{s^{-1}}$	–	ca. 25	0.3	pr	Reaction probably associated with change in number of chloride ligands and/or substitution of Cl^- by H_2O. Measured in the presence of 0.5 mol $\mathrm{dm^{-3}}$ HCl.	Stor...75–1188
17.12	Pt^{III} + Cu^{II} (et)	$(1.5 \pm 0.2) \times 10^8$	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol $\mathrm{dm^{-3}}$ HCl. Cu^{II} in the form of chloro complex.	Stor...75–1188

TABLE 17. Platinum(I) and platinum(III) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/^{\circ}C$	pH	Method	Comments	Ref.
17.13	$Pt^{III} + Pt^{III}$ (dis)	$2k = ca.\ 2 \times 10^9$	0.5 (HCl)	$ca.$ 25	0.3	pr	Rate constant is for the decay of the second transient Pt^{III} species, $(Pt^{III})^{ii}$ in entry 17.11. Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
	Pt^{III} from $PtCl_6{}^{2-} + h\nu$							
17.14	$Pt^{III} + Fe^{2+}$ (et)	$(2.8 \pm 0.3) \times 10^6$	2×10^{-3}	–	–	f.ph.	From dependence of rate constant for this reaction on ionic strength charge on Pt^{III} is –1, and identified therefore as $PtCl_4{}^-$. Broszkiewicz and Grodkowski (ref. 76–1055) suggest however that the reaction observed under the conditions employed was $Cl_2{}^- + Fe^{2+}$. Other experiments give $k = (4.0 \pm 0.6) \times 10^6$ dm^3 mol^{-1} s^{-1} for $Cl_2{}^- + Fe^{2+}$.	Wrig.72–7088
17.15	$Pt^{III} + Pt^{III}$ (dis)	$2k = (4.6 \pm 0.4) \times 10^6$	10^{-3}	$ca.$ 20	5.8	f.ph.	Rate constant calculated taking $\epsilon_{410} = 3.7 \times 10^3$ dm^3 mol^{-1} cm^{-1}.	Wrig.72–7088
	Pt^{III} from $PtCl_4{}^{2-} + OH$							
17.16	(chemical structure)	1.8×10^5 s^{-1}	–	RT	nat	pr	Rate constant measured from decay of reactant at 450 nm.	Adam..68–0169
		2.0×10^5 s^{-1}	–	RT	nat	pr	Rate constant measured from decay of reactant at 450 nm.	Ghos.69–0144
		2.0×10^5 s^{-1}	–	RT	nat	pr	Rate constant measured from build–up of product at 400 nm. Ligand reorganization mechanism implied from similarity of products of $PtCl_4{}^{2-} + OH$ and $PtCl_6{}^{2-} + e_{aq}^-$ (ref. 68–0169).	Adam..68–0169
	Pt^{III} from $Pt(en)_2{}^{2+} + Cl_2{}^-$							
17.17	$(Pt^{III})^i \to (Pt^{III})^{ii}$	$(1.3 \pm 0.1) \times 10^3$ s^{-1}	–	$ca.$ 25	0.3	pr	Decay approximates to two consecutive first order processes (see also 17.18). Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188

TABLE 17. Platinum(I) and platinum(III) reactions — Continued

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
17.18	(Pt^{III})^{ii}→ (Pt^{III})^{iii}	7.7 ± 0.8 s^{-1}	–	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl. See also comments under 17.17.	Stor...75–1188
17.19	Pt^{III} + Cu^{II} (et)	(3.2 ± 0.7) x 10^6	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
17.20	Pt^{III} + Fe^{II} (et)	(2.5 ± 0.4) x 10^5	0.5 (HCl)	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188

Pt^{III} from Pt(en)$_2$$^{2+}$ + OH

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
17.21	(Pt^{III})^i → (Pt^{III})^{ii} + H$^+$	(2.5 ± 0.2) x 10^5 s^{-1}	–	RT	4.0–7.0	pr	–	Brod...76–1093
		(2.4 ± 0.3) x 10^5 s^{-1}	–	RT	7.0–9.6	pr	–	Brod...76–1093
17.22	(Pt^{III})^i + OH$^-$ → (Pt^{III})^{ii} + H$_2$O	(3.1 ± 0.5) x 10^{10}	–	RT	7.0–9.6	pr	–	Brod...76–1093
17.23	(Pt^{III})^i + H$^+$ → (Pt^{III})^{iii}	(4.2 ± 0.9) x 10^9	–	RT	4.0–7.0	pr	–	Brod...76–1093
17.24	(Pt^{III})^{ii} + (Pt^{III})^{ii} (dis?)	(1.5 ± 0.4) x 10^6	–	RT	2.9–8.5	pr	Measured in the presence of (0–2) x 10^{-3} mol dm^{-3} Cl$^-$.	Brod...76–1093
		(4.3 ± 2.8) x 10^6	–	RT	4.0–9.1	f.ph.	Measured in the presence of (0–1) x 10^{-5} mol dm^{-3} Cl$^-$. Unclear whether these rate constants refer to k or $2k$.	Brod...76–1093
17.25	(Pt^{III})^{ii} + Cu^{II}	< 10^4	–	RT	6.3–6.6	pr	–	Brod...76–1093
17.26	(Pt^{III})^{ii} + Fe(CN)$_6$$^{4-}$ (et)	(2.3 ± 0.2) x 10^8	–	RT	6.3–6.6	pr	–	Brod...76–1093
17.27	(Pt^{III})^{ii} + O$_2$	< 10^5	–	RT	6.3–6.6	pr	–	Brod...76–1093
17.28	(Pt^{III})^{iii} → (Pt^{III})^i + H$^+$	(6.6 ± 1.8) x 10^2 or pK_a = 6.8 ± 0.2	–	RT	2.8–4.3	pr	Cf. entry 17.23	Brod...76–1093
17.29	(Pt^{III})^{iii} → ?	28 ± 6 s^{-1}	–	RT	2.8–4.3	pr	Reaction may be second order.	Brod...76–1093
17.30	(Pt^{III})^{ii} + Cl$^-$ → (Pt^{III})^{iv}	(1.11 ± 0.09) x 10^9	–	RT	3–4,5.1	pr	–	Brod...76–1093
17.31	(Pt^{III})^{iv} + Cu^{II} (et?)	(2.7 ± 1.0) x 10^5	–	RT	2.1	pr	Measured in the presence of 5 x 10^{-6} mol dm^{-3} Cl$^-$.	Brod...76–1093
		(3.2 ± 1.1) x 10^5	–	RT	2.0	f.ph.	Measured in the presence of 0–0.5 mol dm^{-3} 2–methyl-2–propanol. Mechanism of reaction may be complex as the rate constants were appreciably higher (25–50%) at the lower [Cu^{II}] employed.	
17.32	(Pt^{III})^{iv} + (Pt^{III})^{iv} (dis?)	$'k' = (5.7 \pm 1.0)$ x 10^7	–	RT	3.4	pr	Measured in the presence of 10^{-5} mol dm^{-3} Cl$^-$. Rate constant calculated taking ϵ_{260} (Pt^{III})^{iv} = 9070 dm^3 mol^{-1} cm^{-1}.	Brod...76–1093

TABLE 17. Platinum(I) and platinum(III) reactions — Continued

No.	Reaction	$k/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
17.32 Cont.		$'k' = (4.9 \pm 1.9) \times 10^7$	–	RT	2.0	f.ph.	Measured in the presence of (0–1) x 10^{-5} mol dm^{-3} Cl^- and 0–0.5 mol dm^{-3} 2–methyl–2–propanol. Rate constant calculated taking $\epsilon_{260}(\text{Pt}^{III})^{iv}$ = 9490 $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. Unclear whether these rate constants refer to k or $2k$.	Brod...76–1093
	Pt^{III} from trans–$Pt(en)_2Cl_2{}^{2+}$ + e_{aq}^- or CH_3COHCH_3							
17.33	Pt^{III} + Pt^{III} (dis)	$2k = (5.8 \pm 1.0) \times 10^7$	–	ca. 25	–	pr	Measured in the presence of 2.6 mol dm^{-3} 2–propanol.	Stor...75–1188
	Pt^{III} from trans–$Pt(en)_2Cl_2{}^{2+}$ + H							
17.34	Pt^{III} + Pt^{III} (dis)	$2k = (8.8 \pm 1.0) \times 10^7$	–	ca. 25	2	pr	Measured in the presence of 0.11–2 mol dm^{-3} 2–methyl–2–propanol.	Stor...75–1188
	Pt^{III} from trans–$Pt(en)_2Cl_2{}^{2+}$ + ·CH_2OH							
17.35	Pt^{III} + Pt^{III} (dis)	$2k = (1.04 \pm 0.38) \times 10^8$	–	ca. 25	–	pr	Measured in the presence of 2–4 mol dm^{-3} methanol.	Stor...75–1188
	Pt^{III} from $Pt(dien)Cl^+$ + Cl_2^-							
17.36	Pt^{III} + Cu^{II} (et)	$(3.2 \pm 0.7) \times 10^8$	–	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
17.37	Pt^{III} + Pt^{III} (dis)	$2k = (6.8 \pm 1.6) \times 10^8$	–	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
	Pt^{III} from $Pt(dien)$ Cl^+ + OH							
17.38	$(Pt^{III})^i \rightarrow (Pt^{III})^{ii}$	$(4.8 \pm 0.8) \times 10^3$	–	RT	nat	pr	Rate constant for initial decay of Pt^{III} transient. This process is followed by (i) an intermediate process exhibiting mixed order kinetics, and (ii) a slow second order decay with $2k = (7.6 \pm 0.6) \times 10^4$ $\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$.	Brod...76–1093
	Pt^{III} from $PtLCl^+$ + Cl_2^- (L = tetraethyldiethylenetriamine).							
17.39	Pt^{III} + Cu^{II}	$(1.5 \pm 0.4) \times 10^7$	–	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
17.40	Pt^{III} + Pt^{III}	$2k = ca. 8 \times 10^5$	–	ca. 25	0.3	pr	Measured in the presence of 0.5 mol dm^{-3} HCl.	Stor...75–1188
	Pt^{III} from $PtLCl^+$ + OH (L = tetraethyldiethylenetriamine).							
17.41	$(Pt^{III})^i \rightarrow (Pt^{III})^{ii}$	1.8 ± 0.6 s^{-1}	–	ca. 25	nat	pr	–	Brod...76–1093

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 18. Rhodium(II) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°\mathrm{C}$	pH	Method	Comments	Ref.
	Rh(NH₃)₄²⁺ and related complexes							
18.1	$Rh(NH_3)_4^{2+} + H_2O \rightarrow$ $Rh(NH_3)_3H_2O^{2+} + NH_3$	$3.5 \times 10^2\ \mathrm{s^{-1}}$	–	RT	4.0	pr	Rate constant measured by change in conductivity resulting from $NH_3 + H^+$ $\rightarrow NH_4^+$. Solutions contained also 0.5 mol dm⁻³ 2–methyl–2–propanol.	Lili..75–1128
18.2	$Rh(NH_3)_3H_2O^{2+} + H_2O \rightarrow$ $Rh(NH_3)_2(H_2O)_2^{2+} + NH_3$	$40\ \mathrm{s^{-1}}$	–	RT	4.0	pr	Rate constant measured by change in conductivity resulting from $NH_3 + H^+$ $\rightarrow NH_4^+$. Solutions contained also 0.5 mol dm⁻³ 2–methyl–2–propanol.	Lili..75–1128
18.3	$Rh(NH_3)_4^{2+} + O_2 \rightarrow$ $O_2Rh(NH_3)_4^{2+}$	3.1×10^6	–	RT	4.0	pr	Product characterised by coductivity measurements. Measured in the presence of 0.5 mol dm⁻³ 2–methyl–2–propanol.	Lili..75–1128
18.4	$Rh(NH_3)_4^{2+} +$ $Rh(NH_3)_4^{2+}$ (dis?)	$2k = ca.\ 1.2 \times 10^7$	–	RT	4.0	pr	Estimated from dependence of chain length in the $Rh(NH_3)_4^{2+} +$ $Rh(NH_3)_4Br_2^+$ reaction on dose rate.	Lili..75–1128
18.5	$Rh(NH_3)_4^{2+} +$ $Rh(NH_3)_4Br_2^+ \rightarrow$ $Rh(NH_3)_4^{3+} + Rh(NH_3)_4Br_2$	$ca.\ 1.4 \times 10^6$	–	RT	4.0	pr	Estimated from initial conductivity change. Measured in the presence of 0.5 mol dm⁻³ 2–methyl–2–propanol. Products inferred from chain reaction which ensues.	Lili..75–1128

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions

No.	Reaction	k/dm^3 mol^{-1} s^{-1} [a]	I	t/°C	pH	Method	Comments	Ref.
	Ru^I							
	Ru(NH$_3$)$_5$N$_2^+$							
19.1	Ru(NH$_3$)$_5$N$_2^+$ + Ru(NH$_3$)$_5$N$_2^+$ (dis)	$2k = 2.7$ x 10^9	≤ 6 x 10^{-4}	20 ± 2	nat	pr	Deposit of metallic ruthenium and molecular nitrogen (G(N$_2$) = 1.25) formed as stable products. Immediate products of reaction unknown.	Baxe.71–0234
	Ru^{II}							
19.2	Ru(NH$_3$)$_5$Cl$^+$ + H$_2$O → Ru(NH$_3$)$_5$H$_2$O^{2+} + Cl$^-$	4.7 ± 0.4 s^{-1}	–	20	nat	pr	Product characterised by its absorption spectrum.	Baxe..70–0178
19.3	Ru(NH$_3$)$_5$H$_2$O^{2+} + Ru(NH$_3$)$_5$Cl^{2+} → Ru(NH$_3$)$_5$Cl$^+$ + Ru(NH$_3$)$_5$H$_2$O^{3+}	1.0 x 10^3	3 x 10^{-4}	20	nat	pr	Products inferred from fact that radiation brings about complete aquation of Ru(NH$_3$)$_5$Cl^{2+}.	Baxe..70–0178
19.4	Ru(NH$_3$)$_5$NO^{2+} + O$_2$ (et or af)	7.6 x 10^6	–	RT	–	pr	–	Armo.75–1049
19.5	Ru(NH$_3$)$_5$NO^{2+} + H$_2$CC(CH$_3$)$_2$OH → Ru(NH$_3$)$_5$NO. CH$_2$C(CH$_3$)$_2$OH^{2+}	3.7 x 10^9	–	RT	1.0–10.3	pr	Measured in the presence of 0.1 – 2.0 mol dm^{-3} 2-methyl-2-propanol. Product characterised by elemental microanalysis, ion exchange chromatography, and uv–visible, ir and nmr spectroscopy.	Armo..75–1077
19.6	Ru(NH$_3$)$_5$NO^{2+} + O$_2$CH$_2$C(CH$_3$)$_2$OH (af or et)	3 x 10^9	–	RT	nat	pr	Measured in the presence of 1 mol dm^{-3} 2-methyl-2-propanol.	Armo..75–1077
	Ru^{III}							
19.7	Ru(NH$_3$)$_5$N$_2^{3+}$ + H$_2$O → Ru(NH$_3$)$_5$OH^{2+} + H$^+$ + N$_2$	250 ± 20 s^{-1}	–	20 ± 2	nat	pr	Measured from decay of Ru(NH$_3$)$_5$N$_2^{3+}$ absorption.	Baxe.71–0234
		270 ± 20 s^{-1}	–	20 ± 2	nat	pr	Measured from the formation of Ru(NH$_3$)$_5$OH^{2+}. Ru product characterised by its absorption spectrum G(N$_2$) = 9.7 (≡ 2 G e_{aq}^- + G_{OH}) measured in γ–radiolysis experiments with N$_2$O saturated solutions.	Baxe.71–0234

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Ru^{IV} (The precise nature of these complexes is uncertain; all were formed by OH oxidation of the corresponding Ru^{III} complex).							
19.8	$Ru(NH_3)_6^{4+}$ + $Ru(NH_3)_6^{4+}$ (dis)	4.5×10^9	3×10^{-3}	20	nat	pr	Unclear whether rate constant refers to k or $2k$. A product of this reaction (possibly $Ru(NH_3)_6^{5+}$) decays by a first order process with $k = 0.75\ \text{s}^{-1}$. Further, slower reactions ensue before the formation of the stable products, and these presumably are due to aquation and hydrolysis reactions.	Baxe..70–0178
19.9	$Ru(NH_3)_5Cl^{3+} \rightarrow$ products	$2.5 \times 10^5\ \text{s}^{-1}$	3×10^{-3}	20	nat	pr	The product of this reaction undergoes two further unimolecular reactions with rate constants of 44 and 0.45 s^{-1}. These are probably associated with aquation and hydrolysis reactions.	Baxe..70–0178

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm 25\%$ (or $\pm 50\%$ for $2k$).

TABLE 20. Samarium(II) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/^\circ C$	pH	Method	Comments	Ref.
	$Sm^{2+}{}_{aq}$							
20.1	$Sm^{2+} + BrO_3^-$ (et)	7.1×10^6	0.015	RT	nat	pr	–	Fara.72–0065
		$(7.0 \pm 0.5) \times 10^7$	0.0375	RT	6	pr	–	Pika..73–1084
20.2	$Sm^{2+} + Co(en)_3^{3+}$	$< 1 \times 10^6$	0.06–1.0	RT	6	pr	–	Fara.73–0107
20.3	$Sm^{2+} + Co(NH_3)_5Br^{2+}$ (et)	3.5×10^7	0.06	RT	6	pr	–	Fara.73–0107
		1.6×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		2.5×10^6	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.4	$Sm^{2+} + Co(NH_3)_5Cl^{2+}$ (et)	3.8×10^7	0.06	RT	6	pr	–	Fara.73–0107
		1.7×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		2.3×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.5	$Sm^{2+} + Co(NH_3)_5CN^{2+}$	$< 3.0 \times 10^6$	0.06	RT	6	pr	–	Fara.73–0107
20.6	$Sm^{2+} + Co(NH_3)F^{2+}$ (et)	2.5×10^7	0.06	RT	6	pr	–	Fara.73–0107
		1.1×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		1.8×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.7	$Sm^{2+} + Co(NH_3)_5H_2O^{3+}$ (et)	6.0×10^6	0.3	RT	–	pr	–	Fara.73–0107
		8.8×10^6	1.0 (NaClO₄)	RT	–	pr	–	Fara.73–0107
		2.6×10^7	1.0 (NaCl)	RT	–	pr	–	Fara.73–0107
20.8	$Sm^{2+} + Co(NH_3)_5I^{2+}$ (et)	5.8×10^7	0.06	RT	6	pr	–	Fara.73–0107
20.9	$Sm^{2+} + Co(NH_3)_5N_3^{2+}$ (et)	7.8×10^7	0.06	RT	6	pr	–	Fara.73–0107
		2.5×10^8	0.5 (NaClO₄)	RT	6	pr	–	Fara.73–0107
20.10	$Sm^{2+} + Co(NH_3)_5NCS^{2+}$	$< 1.0 \times 10^6$	0.06	RT	6	pr	–	Fara.73–0107
		$< 1.0 \times 10^8$	0.5 (NaClO₄)	RT	6	pr	–	Fara.73–0107
20.11	$Sm^{2+} + Co(NH_3)_6^{3+}$ (et)	$< 1.0 \times 10^6$	0.06	RT	6	pr	–	Fara.73–0107
		5.0×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.12	$Sm^{2+} + Co(NH_3)_5OH^{2+}$ (et)	1.5×10^7	0.3	RT	–	pr	–	Fara.73–0107
		5.0×10^7	1.0 (NaClO₄)	RT	–	pr	–	Fara.73–0107
		5.0×10^7	1.0 (NaCl)	RT	–	pr	–	Fara.73–0107
20.13	$Sm^{2+} + CrO_4^{2-}$ (et)	$(4.0 \pm 0.5) \times 10^9$	0.375	RT	6	pr	–	Pika..73–1084
20.14	$Sm^{2+} + Cu^{2+}$ (et)	8.3×10^7	0.015	RT	nat	pr	–	Fara.72–0065
20.15	$Sm^{2+} + H_2O_2$ (et)	3.5×10^7	0.015	RT	nat	pr	–	Fara.72–0065
		$(6.7 \pm 0.3) \times 10^7$	0.375	RT	6	pr	–	Pika..73–1084
20.16	$Sm^{2+} + Eu^{3+}$ (et)	7.5×10^6	0.015	RT	nat	pr	–	Fara.72–0065
20.17	$Sm^{2+} + IO_3^-$ (et)	4.9×10^7	0.015	RT	nat	pr	–	Fara.72–0065
20.18	$Sm^{2+} + MnO_4^-$ (et)	$(4.7 \pm 0.5) \times 10^9$	0.375	RT	6	pr	–	Pika..73–1084
		6.5×10^9	0.015	RT	nat	pr	–	Fara.72–0065
20.19	$Sm^{2+} + NO_2^-$ (et)	1.1×10^9	$\rightarrow 0$	RT	nat	pr	–	Fara.72–0065
		$(1.3 \pm 0.2) \times 10^9$	0.375	RT	6	pr	–	Pika..73–1084
20.20	$Sm^{2+} + NO_3^-$ (et)	$(1.5 \pm 0.2) \times 10^6$	0.375	RT	6	pr	–	Pika..73–1084
		2.0×10^6	0.015	RT	nat	pr	–	Fara.72–0065
20.21	$Sm^{2+} + N_2O$ (et?)	2.0×10^5	0.015	RT	nat	pr	–	Fara.72–0065

TABLE 20. Samarium(II) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
20.22	$Sm^{2+} + O_2$ (af or et)	3.9×10^8	0.015	RT	nat	pr	–	Fara.72–0065
		$(4.2 \pm 0.5) \times 10^8$	0.375	RT	3–6	pr	–	Pika..73–1084
20.23	$Sm^{2+} + OH$ (et)	6×10^9	–	RT	nat	pr	–	Fara.72–0065
		$(6.2 \pm 0.8) \times 10^9$	0.375	RT	3–6	pr	–	Pika..73–1084
20.24	$Sm^{2+} + Ru(NH_3)_5Br^{2+}$ (et)	1.5×10^8	0.06	RT	6	pr	–	Fara.73–0107
20.25	$Sm^{2+} + Ru(NH_3)_5Cl^{2+}$ (et)	1.5×10^8	0.06	RT	6	pr	–	Fara.73–0107
		4.3×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		6.5×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.26	$Sm^{2+} + Ru(NH_3)_5H_2O^{3+}$ (et)	6.5×10^7	0.3	RT	2	pr	–	Fara.73–0107
		1.8×10^8	1.0 (NaClO₄)	RT	2	pr	–	Fara.73–0107
		1.3×10^9	1.0 (NaCl)	RT	2	pr	–	Fara.73–0107
20.27	$Sm^{2+} + Ru(NH_3)_5I^{2+}$ (et)	$ca.\ 10^8$	0.06	RT	6	pr	–	Fara.73–0107
20.28	$Sm^{2+} + Ru(NH_3)_5OH^{2+}$ (et)	4.0×10^7	0.06	RT	6	pr	–	Fara.73–0107
		2.2×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		6.0×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.29	$Sm^{2+} + Ru(NH_3)_6^{3+}$ (et)	2.5×10^7	0.06	RT	6	pr	–	Fara.73–0107
		2.0×10^8	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		8.0×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
20.30	$Sm^{2+} + Yb^{3+}$ (et)	3.0×10^6	0.015	RT	nat	pr	–	Fara.72–0065

[a] If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for $2k$).

TABLE 21. Thallium(0) and (II) reactions

No.	Reaction	$k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [a]	I	$t/{}^\circ C$	pH	Method	Comments	Ref.
	Tl(0)							
	Tl^0_{aq}							
21.1	$Tl^0 + H_2O_2 \rightarrow$ $Tl^+ + OH + OH^-$	5×10^6	–	RT	0.1,5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions.	Fara..71–0036
		$< 10^7$	–	RT	nat	pr	–	Fara..71–0036
21.2	$Tl^0 + HO_2 \rightarrow$ $Tl^+ + HO_2^-$	1.3×10^{10}	–	RT	0.1,5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions.	Fara..71–0036
21.3	$Tl^0 + O_2 \rightarrow$ $Tl^+ + O_2^-$	$(1.0 \pm 0.2) \times 10^7$	–	RT	nat	pr	–	Fara..71–0036
21.4	$Tl^0 + O_2^- \rightarrow$ $Tl^+ + O_2^{2-}$	1.4×10^9	–	RT	5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions.	Fara..71–0036
21.5	$Tl^0 + Tl^+ \rightleftharpoons$ Tl_2^+	$K = 2.3 \times 10^3\,M^{-1}$ $k_f > 10^{10}$	– –	RT RT	6.5 6.5	pr pr	Measured from the effect of $[Tl^+]$ on the absorption due to Tl_2^+.	Cerc..66–0097
21.6	$Tl^0 + Tl^{II} \rightarrow$ $Tl^+ + Tl^I$	$(4.5 \pm 1) \times 10^9$	–	RT	nat	pr	Products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions. No account taken of the hydrolysis of Tl^{2+} (see entry 21.19). No account taken of competing reaction $Tl_2^+ + Tl^{II}$ (see entry 21.12).	Fara..71–0036
21.7	Tl^0 (?) $+ 1,4$–benzo– quinone $\rightarrow Tl^+ + (1,4$–benzo– quinone)$^-$	2.8×10^9	–	*ca.* 25	7.0	pr	Semiquinone product identified by its absorption spectrum.	Rao.75–1032
	Tl_2^+							
21.8	$Tl_2^+ + H_2O_2 \rightarrow$ $2Tl^+ + OH + OH^-$	$(7 \pm 2) \times 10^6$	–	RT	nat	pr	Products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions.	Fara..71–0036
21.9	$Tl_2^+ + N_2O$ (O at or et)	$(1.4 \pm 0.2) \times 10^7$	–	25	nat	pr	γ–radiolysis studies indicate that N_2 is one of the products of this reaction.	Sell72–0844
21.10	$Tl_2^+ + O_2 \rightarrow$ $2Tl^+ + O_2^-$	$(1.0 \pm 0.2) \times 10^7$ 1.2×10^7	– –	RT RT	nat 0.1,5.2	pr γ	– Rate constant and products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions.	Fara..71–0036 Fara..71–0036
21.11	$Tl_2^+ \rightleftharpoons Tl^0 + Tl^+$	see entry 21.5						
21.12	$Tl_2^+ + Tl^{II} \rightarrow$ $3Tl^+$	$(4.4 \pm 0.9) \times 10^9$ $(4.5 \pm 1) \times 10^9$ $(7.5 \pm 1) \times 10^9$	$\rightarrow 0$ 0.0006 0.015	RT RT RT	nat nat nat	pr pr pr	Products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions. No account taken of the hydrolysis of Tl^+ (see entry 21.19.	Cerc..66–0097 Fara..71–0036

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/dm^3\ mol^{-1}\ s^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
21.13	Tl_2^+ + 1,4–dicyano–benzene → $2Tl^+$ + (1,4–dicyanobenzene)$^-$	2.7×10^9	–	RT		pr	Organic product characterised by its absorption spectrum.	Robi.73–0121
	Tl^{II} (Rate constants from pulse radiolysis and flash photolysis experiments only). *Tl$_{aq}^{2+}$ and TlOH$^+$*							
21.14	Tl^{2+} + Co^{2+} ⇌ Tl^+ + Co^{3+}	$k_f = (6.2 \pm 0.5) \times 10^3$	0.75	25	0.6	f.ph.	Evidence for products and equilibrium from conventional kinetic studies.	Falc..74–7625
21.15	Tl^{2+} + Co^{3+} → Tl^{3+} + Co^{2+}	$(9.5 \pm 0.5) \times 10^6$	0.55	22 ± 2	0.3	f.ph.	Evidence for products from conventional kinetic studies.	Falc..75–7093
21.16	Tl^{2+} + Fe^{2+} → Tl^+ + Fe^{2+}	$(2.42 \pm 0.1) \times 10^6$	0.30	14.7	0.6	f.ph.	Evidence for products from conventional kinetic studies.	Falc..75–7093
		$(2.50 \pm 0.1) \times 10^6$	0.30	18.3	0.6	f.ph.		Falc..75–7093
		$(2.53 \pm 0.1) \times 10^6$	0.30	20.7	0.6	f.ph.		Falc..75–7093
		$(2.60 \pm 0.1) \times 10^6$	0.30	24.8	0.6	f.ph.		Falc..75–7093
		$(2.70 \pm 0.1) \times 10^6$	0.30	29.0	0.6	f.ph.		Falc..75–7093
		$(2.73 \pm 0.1) \times 10^6$	0.30	33.9	0.6	f.ph.		Falc..75–7093
		$(2.81 \pm 0.1) \times 10^6$	0.30	36.0	0.6	f.ph.		Falc..75–7093
		$(2.91 \pm 0.1) \times 10^6$	0.30	39.6	0.6	f.ph.		Falc..75–7093
		$E_a = 48 \pm 2\ kJ\ mol^{-1}$	0.30	14–40	0.6	f.ph.		Falc..75–7093
		$(6.7 \pm 0.7) \times 10^6$	1 ($HClO_4$)	23	0	pr		Schw...74–1017
21.17	Tl^{2+} + Fe^{3+} ⇌ Tl^{3+} + Fe^{2+}	$(1.1 \pm 0.15) \times 10^6$	0.30	25	0.6	f.ph.	Evidence for products and equilibrium from conventional kinetic studies.	Falc..74–7625
21.18	Tl^{2+} + HO_2 → Tl^+ + H^+ + O_2	$(2.5 \pm 1) \times 10^9$	–	RT	1	pr	Estimated from initial decay of Tl^{II} in aerated solutions.	Cerc..66–0097
21.19	Tl^{2+} + H_2O ⇌ TlOH$^+$ + H^+	$pK = 4.6 \pm 0.2$	var	21	2–7	pr	Evidence for equilibrium from optical and conductivity measurements.	O'Ne.75–1130
		$k_f = 3.5 \times 10^5\ s^{-1}$	var	21	2–7	pr		
		$k_r = (1.4 \pm 0.5) \times 10^{10}$	var	21	2–7	pr		
21.20	Tl^{2+} + H_2O_2 → Tl^+ + HO_2 + H^+	$(2.8 \pm 0.8) \times 10^7$	–	RT	1	pr	Evidence for products from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions. (see ref. 71–0036).	Cerc..66–0097
21.21	Tl^{2+} + Mn^{2+} → Tl^+ + Mn^{3+}	$(1.9 \pm 0.2) \times 10^4$	0.75	22 ± 3	0.3	f.ph.	Evidence for products from conventional kinetic studies etc. (see ref. 75–7093).	Falc..75–7093
21.22	Tl^{II} + O_2^- → Tl^I + O_2	2×10^{10}	–	RT	5.2	γ	Rate constant and products deduced from H_2O_2 and H_2 yields in γ–irradiated Tl^I solutions. No account taken of hydrolysis of Tl^{2+} (see entry 21.19).	Fara..71–0036
21.23	Tl^{II} + Tl^0	see entry 21.6						
21.24	Tl^{II} + Tl_2^+	see entry 21.12						

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TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
21.25	$Tl^{2+} + Tl^{2+}$ (dis)	$2k = (3.8 \pm 0.6) \times 10^8$	1 (HClO$_4$)	23	0	pr	Measured from decay of Tl^{2+} monitored at 280 nm. Value of ϵ_{280} used to calculate rate constant not given, but is *ca.* 3200 dm^3 mol^{-1} cm^{-1}.	Schw...74–1017
		$2k = (5.2 \pm 0.5) \times 10^8$	0.25	25	1	f.ph.	Measured from decay of Tl^{2+} monitored at 270 nm. Rate constant calculated taking $\epsilon_{270} = 5500$ dm^3 mol^{-1} cm^{-1}. This value was obtained by interpolation from the measured spectrum of Tl^{2+} and the value of $\epsilon_{260} = 5400$ dm^3 mol^{-1} cm^{-1} measured by Cercek *et al* (ref. 66–0097). Note however that this latter value was measured in solutions at pH *ca.* 6.5 and refers therefore to TlOH$^+$ (see entry 21.19).	Falc..74–7625
		$2k = (5.5 \pm 0.5) \times 10^8$	0.25	25	0.6	f.ph.		
		$2k = (9.2 \pm 0.9) \times 10^8$	0.50	25	0.6	f.ph.		
		$2k = (1.3 \pm 0.1) \times 10^9$	1.0	25	0.6	f.ph.		
		$2k = (1.2 \pm 0.1) \times 10^9$	1.0	25	0.3	f.ph.		
		$2k = (1.3 \pm 0.1) \times 10^9$	1.0	25	0	f.ph.		
		$E_a = 7.9 \pm 1.5$ kJ mol^{-1}	–	15–45	–	f.ph.		
		$2k/\epsilon_{270} = (6.1 \pm 0.6) \times 10^4$ cm s^{-1}	1 (HClO$_4$)	25 ± 2	0	f.ph.	Measured in the presence of 5×10^{-3} mol dm^{-3} Tl^{III} and 1×10^{-4} mol dm^{-3} Tl^{I}.	Burc.70–7309
		$2k/\epsilon_{270} = (1.3 \pm 0.2) \times 10^5$ cm s^{-1}	1 (HClO$_4$)	25 ± 2	0	f.ph.	Measured in the presence of 5×10^{-3} mol dm^{-3} Tl^{III} and 5×10^{-2} mol dm^{-3} 2-propanol.	Burc.70–7309
21.26	TlOH$^+$ + TlOH$^+$ (dis)	$2k = (4.6 \pm 1.6) \times 10^9$	*ca.* 0	RT	6.5	pr	Measured from decay of TlOH$^+$ monitored at 260 nm. Rate constant calculated taking $\epsilon_{260} = 5400$ dm^3 mol^{-1} cm^{-1}.	Cerc..66–0097
		$2k = 5 \times 10^9$	–	RT	> 5.5	pr	Extinction coefficient used to calculate rate constant not given.	O'Ne.75–1130
21.27	$Tl^{2+} + \cdot CH_2OH$ (et or af)	$(1.2 \pm 0.3) \times 10^4$	–	23 ± 2	0.43	γ	Estimated from the γ–ray induced chain reaction in Tl^{II} + methanol solutions, taking k(Tl^{II} + Tl^{II}) $= 5.5 \times 10^8$ dm^3 mol^{-1} s^{-1} (see entry 21.25).	Burc.70–0336
21.28	$Tl^{2+} + CH_3C\ HOH$ (et or af)	$(1.5 \pm 0.4) \times 10^4$	–	23 ± 2	0.43	γ	Estimated from the γ–ray induced chain reaction in Tl^{II} + ethanol solutions, taking k(Tl^{II} + Tl^{II}) $= 5.5 \times 10^8$ dm^3 mol^{-1} s^{-1} (see entry 21.25).	Burc.70–0336

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
21.29	Tl^{2+} + CH$_3$COHCH$_3$ (et or af)	$(9.4 \pm 2.3) \times 10^3$	–	23 ± 2	0.43	γ	Estimated from the γ–ray induced chain reaction in Tl^{II} + 2–propanol solutions, taking k(Tl^{II} + Tl^{II}) $= 5.5 \times 10^8$ dm^3 mol^{-1} s^{-1} (see entry 21.25).	Burc.70–0336
21.30	Tl^{2+} + anisole → Tl$^+$ + (anisole)$^+$	$(5.0 \pm 0.5) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171
21.31	Tl^{2+} + 1,2–dimethoxybenzene → Tl$^+$ + (1,2–dimethoxybenzene)$^+$	$(6.0 \pm 0.6) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171 O'Ne..75–1086
21.32	TlOH$^+$ + 1,2–dimethoxybenzene → Tl$^+$ + OH$^-$ + (1,2–dimethoxybenzene)$^+$	1.2×10^9	–	RT	> 4.7	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1086
21.33	Tl^{2+} + 1,3–dimethoxybenzene → Tl$^+$ + (1,3–dimethoxybenzene)$^+$	$(8.0 \pm 0.8) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171
21.34	Tl^{2+} + 1,4–dimethoxybenzene → Tl$^+$ + (1,4–dimethoxybenzene)$^+$	$(6.5 \pm 0.7) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1086 O'Ne..75–1171
21.35	TlOH$^+$ + 1,4–dimethoxybenzene → Tl$^+$ + OH$^-$ + (1,4–dimethoxybenzene)$^+$	4.5×10^8	–	RT	> 4.7	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1086
21.36	TlOH$^+$ + menaquinone	slow	–	RT	6.8	pr	–	Rao.73–1047
21.37	Tl^{2+} +1,2,3–trimethoxybenzene → Tl$^+$ + (1,2,3–trimethoxybenzene)$^+$	$(3.2 \pm 0.3) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171
21.38	Tl^{2+} + 1,2,4–trimethoxybenzene → Tl$^+$ + (1,2,4–trimethoxybenzene)$^+$	$(6.8 \pm 0.7) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171
21.39	Tl^{2+} + 1,3,5–trimethoxybenzene → Tl$^+$ + (1,3,5–trimethoxybenzene)$^+$	$(7.0 \pm 0.7) \times 10^8$	–	20 ± 2	4	pr	Radical cation product characterised by its absorption and esr spectra.	O'Ne..75–1171

TABLE 21. Thallium(0) and (II) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Tl^{II} chloro–complexes							
21.40	Tl^{2+} + Cl$^-$ ⇌ TlCl$^+$	$K = (6.2 \pm 0.7)$ x 10^4 dm^3 mol^{-1}	1 (HClO$_4$)	23	0	pr	Measured from effect of [Cl$^-$] on absorption spectrum of Tl^{II}.	Dods.74–1038
		$k_f = 9$ x 10^9	1 (HClO$_4$)	23	0	pr	Measured from rate of attainment of equilibrium.	Dods.74–1038
		$k_r = 1.4$ x 10^5 s^{-1}	1 (HClO$_4$)	23	0	pr		
21.41	TlCl$^+$ + Cl$^-$ ⇌ TlCl$_2$	$K = (1.9 \pm 0.4)$ x 10^3 dm^3 mol^{-1}	1 (HClO$_4$)	23	0	pr	Measured from effect of [Cl$^-$] on absorption spectrum of Tl^{II}.	Dods.74–1038
21.42	TlCl$_2$ + Cl$^-$ ⇌ TlCl$_3^-$	$K = 13 \pm 3$ dm^3 mol^{-1}	1 (HClO$_4$)	23	0	pr	Measured from effect of [Cl$^-$] on absorption spectrum of Tl^{II}.	Dods.74–1038
21.43	Tl^{II} + Tl^{II} (dis)	$2k = 5.38$ x 10^9	1	23	0	pr	[Cl$^-$] = 1 x 10^{-3} mol dm^{-3}	Dods.74–1038
		$2k = 5.58$ x 10^9	1	23	0	pr	[Cl$^-$] = 9.7 x 10^{-3} mol dm^{-3}	Dods.74–1038
		$2k = 4.74$ x 10^9	1	23	0	pr	[Cl$^-$] = 0.1 mol dm^{-3}	Dods.74–1038
		$2k = 3.70$ x 10^9	1	23	0	pr	[Cl$^-$] = 0.98 mol dm^{-3}	Dods.74–1038

Plus data at intermediate chloride concentrations.

[a]If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

TABLE 22. Thulium(II) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Tm$_{aq}^{2+}$							
22.1	Tm^{2+} + OH (et)	(7 ± 1) x 10^9	–	RT	3–6	pr	–	Pika..73–1084

[a]If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).
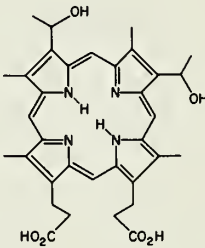
TABLE 23. Ytterbium(II) reactions

No.	Reaction	k/dm³ mol⁻¹ s⁻¹ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	Yb_{aq}^{2+} (Rate constants from pulse radiolysis studies only).							
23.1	$Yb^{2+} + BrO_3^-$	$< 10^5$	0.015	RT	nat	pr	–	Fara.72–0065
23.2	$Yb^{2+} + Co(en)_3^{3+}$	$< 5 \times 10^3$	0.06–1.0	RT	6	pr	–	Fara.73–0107
23.3	$Yb^{2+} + Co(NH_3)_5Br^{2+}$ (et)	3.0×10^6	0.06	RT	6	pr	–	Fara.73–0107
		1.4×10^7	1.0 (NaClO₄)	RT	6	pr		Fara.73–0107
		2.5×10^7	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
23.4	$Yb^{2+} + Co(NH_3)_5Cl^{2+}$ (et)	4.3×10^5	0.06	RT	6	pr	–	Fara.73–0107
		1.9×10^7	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		2.3×10^7	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
23.5	$Yb^{2+} + Co(NH_3)_5CN^{2+}$ (et)	3.0×10^5	0.06	RT	6	pr	–	Fara.73–0107
23.6	$Yb^{2+} + Co(NH_3)_5F^{2+}$ (et)	1.1×10^7	0.06	RT	6	pr	–	Fara.73–0107
		6.0×10^7	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		1.0×10^5	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
23.7	$Yb^{2+} + Co(NH_3)_5H_2O^{3+}$ (et)	2.2×10^5	0.3	RT	2	pr	–	Fara.73–0107
		6.4×10^5	1.0 (NaClO₄)	RT	2	pr	–	Fara.73–0107
23.8	$Yb^{2+} + Co(NH_3)_5N_3^{2+}$ (et)	1.6×10^7	0.06	RT	6	pr	–	Fara.73–0107
		2.6×10^7	0.5 (NaClO₄)	RT	6	pr	–	Fara.73–0107
23.9	$Yb^{2+} + Co(NH_3)_5NCS^{2+}$	$< 5.0 \times 10^4$	0.5 (NaClO₄)	RT	6	pr	–	Fara.73–0107
23.10	$Yb^{2+} + Co(NH_3)_6^{3+}$	$< 5.0 \times 10^4$	0.06	RT	6	pr	–	Fara.73–0107
23.11	$Yb^{2+} + Co(NH_3)_5OH^{2+}$ (et)	7.7×10^6	0.3	RT	5.5	pr	–	Fara.73–0107
		1.9×10^7	1.0 (NaClO₄)	RT	5.5	pr	–	Fara.73–0107
		2.9×10^7	1.0 (NaCl)	RT	5.5	pr	–	Fara.73–0107
23.12	$Yb^{2+} + Cu^{2+}$ (et)	1.2×10^7	0.015	RT	nat	pr	–	Fara.72–0065
23.13	$Yb^{2+} + H_2O_2$ (et)	9.1×10^5	0.015	RT	nat	pr	–	Fara.72–0065
23.14	$Yb^{2+} + IO_3^-$ (et)	2.1×10^5	0.015	RT	nat	pr	–	Fara.72–0065
23.15	$Yb^{2+} + MnO_4^-$ (et)	8.3×10^7	0.015	RT	nat	pr	–	Fara.72–0065
23.16	$Yb^{2+} + NO_2^-$ (et)	4.7×10^7	0.015	RT	nat	pr	–	Fara.72–0065
23.17	$Yb^{2+} + NO_3^-$ (et)	3.6×10^5	0.015	RT	nat	pr	–	Fara.72–0065
23.18	$Yb^{2+} + N_2O$ (et?)	$ca.\ 10^4$	0.015	RT	nat	pr	–	Fara.72–0065
23.19	$Yb^{2+} + O_2$ (et or af)	$(6.3 \pm 1) \times 10^7$	0.375	RT	2	pr	–	Pika..73–1084
		6.5×10^7	0.015	RT	nat	pr	–	Fara.72–0065
23.20	$Yb^{2+} + OH$ (et)	3×10^9	0.015	RT	nat	pr	–	Fara.72–0065
		$(3.2 \pm 0.3) \times 10^9$	0.375	RT	2	pr	–	Pika..73–1084
23.21	$Yb^{2+} + Ru(NH_3)_5Br^{2+}$ (et)	3.3×10^7	0.06	RT	6	pr	–	Fara 73–0107
23.22	$Yb^{2+} + Ru(NH_3)_5Cl^{2+}$ (et)	1.5×10^7	0.06	RT	6	pr	–	Fara.73–0107
		1.8×10^5	1.0 (NaClO₄)	RT	6	pr	–	Fara.73–0107
		2.8×10^5	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107

TABLE 23. Ytterbium(II) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°\mathrm{C}$	pH	Method	Comments	Ref.
23.23	Yb^{2+} + $Ru(NH_3)_5H_2O^{3+}$	1.0×10^7	0.3	RT	2	pr	–	Fara.73–0107
	(et)	2.9×10^7	1.0 (NaClO$_4$)	RT	2	pr	–	Fara.73–0107
		3.2×10^8	1.0 (NaCl)	RT	2	pr	–	Fara.73–0107
23.24	Yb^{2+} + $Ru(NH_3)_5I^{2+}$ (et)	$ca.\ 10^8$	0.06	RT	6	pr	–	Fara.73–0107
23.25	Yb^{3+} + $Ru(NH_3)_6^{3+}$ (et)	5.0×10^6	0.06	RT	6	pr	–	Fara.73–0107
		4.5×10^7	1.0 (NaClO$_4$)	RT	6	pr	–	Fara.73–0107
		3.0×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107
23.26	Yb^{2+} + $Ru(NH_3)_5OH^{2+}$	1.3×10^7	0.06	RT	6	pr	–	Fara.73–0107
	(et)	2.3×10^7	0.3	RT	6	pr	–	Fara.73–0107
		5.0×10^7	1.0 (NaClO$_4$)	RT	6	pr	–	Fara.73–0107
		1.4×10^8	1.0 (NaCl)	RT	6	pr	–	Fara.73–0107

[a]If the data source gives no errors none are shown here but they should be assumed to be at least $\pm25\%$ (or $\pm50\%$ for 2 k).

TABLE 24. Zinc(I) reactions

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/°C$	pH	Method	Comments	Ref.
	$Zn^+{}_{aq}$							
24.1	$Zn^+ + BrO_3{}^-$ (et)	$(2.1 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	–	Meye.68–0855
24.2	$Zn^+ + Cd^{2+}$ (et?)	$< 1 \times 10^7$	0.08	RT	nat	pr	The reason for the discrepancy between these two values is not clear.	Meye.68–0855
		8.3×10^8	–	RT	nat	pr		Baxe..66–0848
24.3	$Zn^+ + ClO_3{}^-$	$< 3 \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
24.4	$Zn^+ + Co^{2+}$	$< 3 \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
24.5	$Zn^+ + Co(bpy)_3{}^{3+}$ (et)	2.6×10^9	–	RT	nat	pr	–	Baxe..72–0381
24.6	$Zn^+ + Co(en)_3{}^{2+}$ (et)	$(2.5 \pm 0.4) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.7	$Zn^+ + cis\text{–}Co(en)_2Cl_2{}^+$ (et)	$(1.91 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.8	$Zn^+ + trans\text{–}Co(en)_2Cl_2{}^+$ (et)	$(2.3 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.9	$Zn^+ + Co(en)_2CO_3{}^+$ (et)	$(4.7 \pm 0.7) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.10	$Zn^+ + cis\text{–}Co(en)_2F_2{}^+$ (et)	$(5.4 \pm 0.8) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.11	$Zn^+ + Co(en)_2FH_2O^{2+}$ (et)	$(4.7 \pm 0.7) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.12	$Zn^+ + cis\text{–}Co(en)_2NH_3Cl^{2+}$ (et)	$(1.47 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.13	$Zn^+ + cis\text{–}Co(en)_2NH_3NO_2{}^{2+}$ (et)	$(2.7 \pm 0.7) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.14	$Zn^+ + Co(NH_3)_6{}^{3+}$ (et)	$(8.4 \pm 1.3) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0248
24.15	$Zn^+ + Co(NH_3)_5Br^{2+}$ (et)	$(2.6 \pm 0.4) \times 10^9$	0.08	RT	4.0	pr	–	Meye.69–0428
24.16	$Zn^+ + Co(NH_3)_5Cl^{2+}$ (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.17	$Zn^+ + Co(NH_3)_5CN^{2+}$ (et)	$(1.30 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.18	$Zn^+ + Co(NH_3)_5F^{2+}$ (et)	$(8.2 \pm 1.2) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.19	$Zn^+ + Co(NH_3)_5fumar\text{-}ate^+$ (et)	$(1.2 \pm 0.3) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.20	$Zn^+ + Co(NH_3)_5H_2O^{3+}$ (et)	$(1.56 \pm 0.2) \times 10^9$	0.08	RT	4.0	pr	–	Meye.69–0428
24.21	$Zn^+ + Co(NH_3)_5OH^{2+}$ (et)	$(1.10 \pm 0.2) \times 10^9$	0.08	RT	6.6	pr	–	Meye.69–0428
24.22	$Zn^+ + Co(NH_3)_5N_3{}^{2+}$ (et)	$(1.49 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.23	$Zn^+ + Co(NH_3)_5NCS^{2+}$ (et)	$(1.65 \pm 0.2) \times 10^9$	0.08	RT	5–6	pr	–	Meye.69–0428
24.24	$Zn^+ + Co(NH_3)_5OOCCH_3{}^{2+}$ (et)	$(5.0 \pm 0.8) \times 10^8$	0.08	RT	5–6	pr	–	Meye.69–0428
24.25	$Zn^+ + Cr^{3+}$	$< 10^7$	–	RT	nat	pr	–	Baxe..66–0848
24.26	$Zn^+ + Cr_2O_7{}^{2-}$ (et)	$(1.6 \pm 0.2) \times 10^{10}$	0.020*	25±2	nat	pr	–	Buxt..76–1072
24.27	$Zn^+ + Cu^{2+}$ (et)	$(2.5 \pm 0.4) \times 10^8$	0.08	RT	nat	pr	–	Meye.68–0855
		$(9.5 \pm 2.0) \times 10^9$	0.4 (ZnSO$_4$)	RT	5–8	γ	Measured by competition with $NO_3{}^-$. Rate constant calculated taking $k(Zn^+ + NO_3{}^-) = 2.1 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (see entry 24.33).	Fiti70–0117
24.28	$Zn^+ + H_2O_2 \rightarrow$ $Zn^{2+} + OH + OH^-$	$(1.80 \pm 0.3) \times 10^9$	–	RT	nat	pr	–	Meye.68–0855
		$(2.3 \pm 0.2) \times 10^9$	–	25±2	nat	pr	Products inferred from γ–radiolysis experiments (see ref. 73–0039).	Buxt..76–1072
		$E_a = 10.5 \pm 1.0$ kJ mol^{-1}	–	–	nat	pr	–	Buxt..76–1072

TABLE 24. Zinc(I) reactions — Continued

No.	Reaction	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [a]	I	$t/^\circ C$	pH	Method	Comments	Ref.
24.29	$Zn^+ + H_3O^+$	$< 10^6$	0.08	RT	–	pr	–	Meye.68–0855
24.30	$Zn^+ + IO_3^-$ (et)	$(3.6 \pm 0.5) \times 10^9$	0.08	RT	nat	pr	–	Meye.68–0855
		$(1.7 \pm 0.3) \times 10^{10}$	0.4 (ZnSO$_4$)	RT	5–8	γ	Measured by competition with NO_3^-. Rate constant calculated taking $k(Zn^+ + NO_3^-) = 2.1 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (see entry 24.33).	Fiti70–0117
24.31	$Zn^+ + Ni^{2+}$ (et)	$< 5 \times 10^6$	0.08	RT	nat	pr	–	Meye.68–0855
		5×10^7	–	RT	nat	pr	–	Baxe..66–0848
24.32	$Zn^+ + NO_2^-$ (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	nat	pr		Meye.68–0855
24.33	$Zn^+ + NO_3^-$ (et)	$(2.1 \pm 0.3) \times 10^9$	0.08	RT	nat	pr		Meye.68–0855
24.34	$Zn^+ + N_2O \rightarrow$ $ZnO^+ + N_2$	$< 1.3 \times 10^7$	–	RT	nat	pr	–	Meye.68–0855
		$(3.7 \pm 0.4) \times 10^7$	–	25±2	nat	pr	Products characterised by their absorption spectrum (see ref. 76–1072) and in γ–radiolysis experiments (see ref. 73–0039).	Buxt..76–1072
		$E_a = 35.5 \pm 1.4\ \mathrm{kJ\ mol^{-1}}$	–	1–30	nat	pr		
24.35	$Zn^+ + O_2 \rightarrow$ $Zn^{2+} + O_2^-$	$(2.4 \pm 0.4) \times 10^9$	–	RT	nat	pr	–	Meye.68–0855
		3.3×10^9	–	RT	nat	pr	–	Baxe..66–0848
							Products characterised by their absorption spectrum (see ref. 76–1072) and reactivity with 1,4–benzoquinone (see ref. 76–1134).	
24.36	$Zn^+ + OH$ (et)	5.7×10^9	–	RT	nat	pr	No correction made for competing reaction $Zn^+ + Zn^+$.	Baxe..66–0848
		$ca.\ 8 \times 10^9$	–	25±2	nat	pr	Estimated from decay of Zn^+ in the absence of OH scavengers taking into account competing reactions such as $Zn^+ + Zn^+$, $Zn^+ + H_2O_2$, OH + OH etc.	Buxt.75–1027
24.37	$Zn^+ + Pb^{2+}$ (et)	4.0×10^8	–	RT	nat	pr	–	Baxe..66–0848
24.38	$Zn^+ + Ru(bpy)_3^{3+}$ (et)	2.5×10^9	–	RT	nat	pr	–	Baxe.72–0381
24.39	$Zn^+ + Ru(NH_3)_6^{3+}$ (et)	$(2.2 \pm 0.3) \times 10^9$	0.08	RT	nat	pr	–	Navo.70–1229
24.40	$Zn^+ + S_2O_8^{2-} \rightarrow$ $Zn^{2+} + SO_4^- + SO_4^{2-}$	$(1.3 \pm 0.1) \times 10^9$	0.02*	25±2	nat	pr	–	Buxt..76–1072
24.41	$Zn^+ + Zn^+$	$2k < 8 \times 10^8$	0.4	25±2	nat	pr	Estimated from rate of decay of Zn^+ in the presence of 2–methyl–2–propanol. Major competing reaction is $Zn^+ + \cdot CH_2C(CH_3)_2OH$.	Buxt.75–1027
24.42	$Zn^+ + $ allyl alcohol $\rightarrow$ (Zn – allyl alcohol)$^+$	$ca.\ 10^8$	–	25±2	nat	pr	Product characterized by its absorption spectrum.	Buxt..76–1072

TABLE 24. Zinc(I) reactions — Continued

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
24.43	Zn^+ + benzophonone → Zn^{2+} + (benzophenone)$^-$	2.5×10^9	–	RT	7.0	pr	Measured in the presence of *ca.* 1 mol dm^{-3} 2–methyl–2–propanol. Ketyl radical product characterised by its absorption spectrum.	Rao.75–1032
24.44	Zn^+ + 1,4–benzo– quinone → Zn^{2+} + (1,4–benzoquinone)$^-$	$(3.0 \pm 0.6)\,10^9$	–	25±2	5.7	pr	Measured in the presence of 1 mol dm^{-3} 2–methyl–2– propanol. Semi– quinone product characterised by its absorption spectrum.	Sell.76–1134
		4.8×10^9	–	RT	7.0	pr	Measured in the presence of *ca.* 1 mol dm^{-3} 2– methyl–2–propanol.	Rao.75–1032
24.45	Zn^+ + menaquinone → Zn^{2+} + (menaquinone)$^-$	$(3.8 \pm 0.4) \times 10^9$	–	RT	7.1	pr	Measured in the presence of *ca.* 1 mol dm^{-3} 2–methyl– 2–propanol. Semi– quinone product characterised by its absorption spectrum.	Rao.73–1047, Rao.75–1032

Zn^I Complexes

ZnL^+ (from ZnL^{2+} + $CH_3CO^-CH_3$), L = hematoporphyrin (ix) (no reference made to number of protons involved with complex).

No.	Reaction	$k/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ [a]	I	$t/^\circ\text{C}$	pH	Method	Comments	Ref.
24.46	ZnL^+ + ZnL^+ → $(ZnL)_2^{2+}$	$'k' = (2.1 \pm 0.4) \times 10^8$	0.1	RT	13	pr	Unclear whether k or $2k$. Measured in the presence of 1 mol dm^{-3} 2–pro– panol. Dimerisation mechanism implied from subsequent reactions (see entry 24.47) and comparison with the products of reduction of ZnL^{2+} in aprotic solvents.	Hare.74–1040
24.47	$(ZnL)_2^{2+}$ → P	$17 \pm 2\ \text{s}^{-1}$	0.1	RT	13	pr	Reaction suggested to involve internal rearrangement.	Hare.74–1040
	P → dihydroporphyrin product	$< 0.14\ \text{s}^{-1}$	0.1	RT	13	pr	Reaction presumed to involve splitting of dimer.	Hare.74–1040

[a] If the data source gives no errors none are shown here but they should be assumed to be at least ±25% (or ±50% for 2k).

No.	Reaction	k/s^{-1} [b]	I	$t/°C$	pH	Method	Comments	Ref.
	Electron adducts							
25.1	$(NH_3)_5Co^{III}(p-OOCC_6H_4NO_2)^- \rightarrow$ $(NH_3)_5Co^{II}(p-OOCC_6H_4NO_2)$	2.6×10^3	–	RT	7.0	pr	–	Simi..77–1027
25.2	$(NH_3)_5Co^{III}(m-OOCC_6H_4NO_2)^- \rightarrow$ $(NH_3)_5Co^{II}(m-OOCC_6H_4NO_2)$	1.5×10^2	–	RT	7.0	pr	–	Simi..77–1027
25.3	$(NH_3)_5Co^{III}(o-OOCC_6H_4NO_2)^- \rightarrow$ $(NH_3)_5Co^{II}(o-OOCC_6H_4NO_2)$	4.0×10^5	–	RT	7.0	pr	–	Simi..77–1027
25.4	$(NH_3)_5Co^{III}(o-OOCC_6H_4NO_2H) \rightarrow$ $(NH_3)_5Co^{II}(o-OOCC_6H_4NO_2) + H^+$	9.5×10^3	–	RT	0.8	pr	–	Simi..77–1027
25.5	$(NH_3)_5Co^{III}[2,4-OOCC_6H_4(NO_2)_2]^-$ $\rightarrow (NH_3)_5Co^{II}[2,4-OOCC_6H_4(NO_2)_2]$	3.5×10^4	–	RT	7.0	pr	–	Simi..77–1027
25.6	$(NH_3)_5Co^{III}[3,5-OOCC_6H_4(NO_2)_2]^-$ $\rightarrow (NH_3)_5Co^{II}[3,5-OOCC_6H_4(NO_2)_2]$	1.3×10^2	–	RT	7.0	pr	–	Simi..77–1027
25.7	$Cu^{II}(gluthathione^-) \rightarrow$ $Cu^I(gluthathione)$	(3.6 ± 0.3) $\times 10^3$	–	RT	11	pr	Rate constant independent of $[Cu^{II}]$: [glu-tathione] ratio in range 1:2 to 1:5 and of $[Cu^{II}]$ in the range $(1–10) \times 10^{-4}$ mol dm^{-3}.	Fara.76–1016
25.8	$Cu^{II}(gly)_2(gly^-) \rightarrow$ $Cu^I(gly)_3$	(1.7 ± 0.3) $\times 10^4$	–	RT	9	pr	Rate constant independent of $[Cu^{II}]$: [gly] ratio in range 1:6 to 1:15 and of $[Cu^{II}]$ in the range $(1–10) \times 10^{-4}$ mol dm^{-3}.	Fara.76–1016
	Hydroxyl radical adducts							
25.9	$(NH_3)_5Co^{III}OOCC_6H_5OH \rightarrow$ $(NH_3)_5Co^{II}OOCC_6H_4OH + H^+$	$< 10^2$	–	RT	6.0	pr	–	Cohe.71–0282
	Hydrogen atom adducts							
25.10	$(NH_3)_5Co^{III}OOCC_6H_5H \rightarrow$ $(NH_3)_5Co^{II}OOCC_6H_4H + H^+$	$< 10^2$	–	RT	1	pr	–	Cohe.71–0282

[a]Intramolecular electron transfer reactions of metallo–proteins and related systems *not* included..

[b]N.B. First order rate constants.

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Kinetic data have been compiled for reactions of uncommon oxidation states of metals which are produced by radiolysis of aqueous solutions of metal ions. Most of the reaction rates are for transient species, and the rates were determined by pulse radiolysis; some data were obtained by flash photolysis and gamma radiolysis. Metal ions from Groups IB, IIB, IIIA, IVA, VIB, VIIB, VIIIB, and the lanthanides are included in the compilation.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Aqueous solution; chemical kinetics; complex ions; electron transfer; metal ions; radiation chemistry; rates; transients.

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NOTE: At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash., D.C. 20056.

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